Atomic Structure

The section of the general chemistry course that deals with atomic structure is designed to describe in qualitative terms the current understanding of the fundamental structure of all matter. Here, atoms are introduced as the basic building blocks of matter. The composition of the atom is described. Frequently, the fundamental experiments that led to the discovery of electrons, protons, and neutrons are laid out in some detail.

The development of quantum mechanics enabled chemists to describe electron energies and locations outside the nucleus more accurately than was possible with the planetary model for the atom. The meanings and implications of quantum numbers, photons, electromagnetic radiation, and radial probability distributions are central to describing the atom in terms of quantum mechanics. Other central ideas include the *aufbau* principle and the uncertainty principle.

Symbolic representations of atomic structure and three-dimensional representations of electron probability regions enable chemists to deal with the behavior of atoms in terms of current atomic theory and to communicate chemical information more clearly.

Study Questions

AS-1. An atom of strontium–90, $^{90}_{38}\text{Sr}$, contains

(A) 38 electrons, 38 protons, 52 neutrons.

(B) 38 electrons, 38 protons, 90 neutrons.

(C) 52 electrons, 52 protons, 38 neutrons.

(D) 52 electrons, 38 protons, 38 neutrons.

Knowledge Required: (1) The symbolic representation of isotopes, with the atomic number of an element written as a left-hand subscript, the mass number written as a left-hand superscript, and the ionic charge (if any) written as a right-hand superscript. (2) The fact that the mass number is the sum of the number of protons and neutrons.

Thinking it Through: The atomic number of 38 indicates 38 protons, eliminating choice **(C)**. This is a neutral atom, so there are also 38 electrons, eliminating choice **(D)**. The mass number of 90 for strontium eliminates choice **(B)**, which corresponds to a mass number of 128. The correct number of neutrons is found by subtracting the atomic number (38) from the mass number (90) giving a value of 52, which is found in choice **(A)**. *Note*: There is redundant information in this question; the term "strontium–90" gives the same information as the symbolic representation, $^{90}_{38}\text{Sr}$ if you know the symbol for strontium and can find its atomic number on the periodic table.

AS-2. What do these have in common?

^{20}Ne $\quad$ $^{19}\text{F}^-$ $\quad$ $^{24}\text{Mg}^{2+}$

(A) the same number of protons

(B) the same number of neutrons

(C) the same number of electrons

(D) the same size

Knowledge Required: (1) The symbolic representation of isotopes, with the atomic number of an element written as a left-hand subscript, the mass number written as a left-hand superscript, and the ionic charge (if any) written as a right-hand superscript. (2) The fact that the mass number is the sum of the number of protons plus neutrons.

Thinking it Through: The periodic table contains the atomic number of each element, which indicates both the number of protons in the nucleus and the number of electrons *for a neutral atom*. Negative ions have one or more additional electrons, and positive ions are short by one or more electrons. Also, subtracting the atomic number from the mass number gives the number of neutrons. These three species have different atomic numbers (10, 9, and 12), so the number of protons cannot be the same, eliminating choice **(A)**. Subtracting each atomic number from the given mass number (20, 19, and 24) gives different numbers of neutrons in each case (10, 10, and 12), eliminating choice **(B)**. Considering the number of electrons, the neutral atom neon has 10; fluorine has 9 in a neutral atom—and 10 in a fluoride ion; magnesium has 12 in a neutral atom—and 10 in a +2 magnesium ion. The number of electrons is thus the same for all three. Such species are called *isoelectronic*. Note that Na^+, O^{2-}, and Al^{3+} are also isoelectronic with the given species. Choice **(D)** cannot be true; because, given equal numbers of electrons, those nuclei with greater positive charge will attract electrons more strongly than those with less positive charge.

AS-3. Which pair represents isotopes?

(A) ${}^{54}_{24}Cr$ and ${}^{54}_{26}Fe$ **(B)** ${}^{235}_{92}U$ and ${}^{238}_{92}U$

(C) ${}^{116}_{48}Cd$ and ${}^{116}_{50}Sn$ **(D)** ${}^{239}_{93}Np$ and ${}^{239}_{94}Pu$

Knowledge Required: The definition of "isotope," and the associated symbolic representation.

Thinking it Through: Isotopes are forms of the same element that differ only in the number of neutrons in their nuclei. The identity of an element is determined by the number of protons (the atomic number), which is represented by the left-hand subscript. Choice **(B)**, the only choice with the same element symbol for both atoms, also has the identical atomic number (92). The other three choices have identical mass numbers, which simply means that the sum of protons plus neutrons is the same for each one. *Note*: The similar terms, *isotope*, *isomer*, and *allotrope* are often confused.

AS-4. Which particle, if lost from the nucleus, will ***not*** result in a change in the atomic number?

(A) proton **(B)** alpha particle

(C) beta particle **(D)** neutron

Knowledge Required: (1) The general composition of atomic nuclei (numbers of neutrons and protons). (2) The modes of radioactive decay available to nuclei. (3) The meanings of the terms alpha particle and beta particle.

Thinking it Through: Any of these particles could be lost from the nucleus during a nuclear (not chemical) change. Since the atomic number is determined by the number of positively charged protons in the nucleus, emission of *any* charged particle would change the atomic number. A proton, choice **(A)**, has one unit of positive charge. An alpha particle, choice **(B)**, has two units of positive charge. A beta particle, choice **(C)**, has one unit of negative charge. The only remaining choice is the neutron, which has no charge, and therefore does not change the atomic number.

AS-5. When alpha particles were shot at a metal foil target to probe the structure of the atom, most of the particles passed through without any deflection in path. Some particles were deflected at large angles. This indicated to Rutherford that

(A) the metal foil was continuous matter.

(B) the mass of the metal atoms was spread out evenly.

(C) the atoms of the metal were mostly empty space.

(D) the alpha particles had great penetrating power.

Knowledge Required: The general features of Ernest Rutherford's alpha-particle-scattering experiment.

Thinking it Through: Prior to Rutherford's classic scattering experiment, atoms were thought to consist of a cloud of positive charge with electrons embedded throughout. Rutherford discovered that some alpha particles were scattered at large angles. The only explanation was that most of the mass and all of the positive charge had to be concentrated in a tiny fraction of the volume of atom. The rest of the atom had to be mostly empty space. Choice **(B)** describes atomic theory *before* Rutherford's experiment. Choice **(A)** suggests that atoms do not exist at all. Choice **(D)** does not bear directly on Rutherford's experiment. The large scattering angles of the alpha particles were *only* consistent with an atomic model in which the positive charge and almost all of the mass were concentrated in a small, dense center. The rest of the atom had to be mostly empty space, choice **(C)**.

AS-6. An atom has a valence shell electron configuration of ns^1. To which group of elements in the periodic table does it belong?

(A) transition elements

(B) lanthanides

(C) alkaline earth metals

(D) alkali metals

Knowledge Required: (1) The symbolic representation of electron configuration. (2) The meaning of the term "valence shell." (3) The names associated with particular families or periods in the periodic table. (4) The ability to correlate symbolic representations with locations in the periodic table.

Thinking it Through: Elements having ns^1 as the valence-shell-electron configuration have a single electron in the *s* orbital. Such elements include H ($1s^1$), Li ($2s^1$), Na ($3s^1$), and K ($4s^1$). These are the ***alkali metals***, found in Group IA of the periodic table, choice **(D)**. The alkaline earth metals, Group IIA, all have electron configurations of ns^2, choice **(C)**. Transition elements, choice **(A)**, and lanthanides, choice **(B)**, have varying numbers of valence electrons. Their characteristic valence electron configurations are $ns^2(n-1)d^x$ and $ns^2(n-1)d^x\ (n-2)f^y$ respectively. The maximum value of x is 10 and the maximum value of y is 14.

AS-7. The energy of a photon is greatest in the case of

(A) X-rays.

(B) ultraviolet radiation

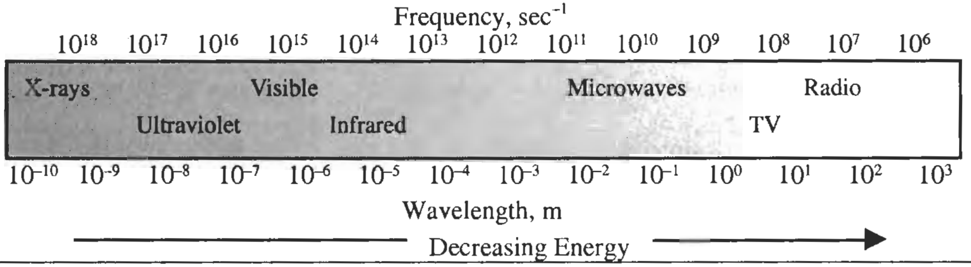
(C) visible light.

(D) infrared radiation.

Knowledge Required: (1) The meaning of the term "photon." (2) The names associated with regions of the electromagnetic spectrum. (3) The qualitative knowledge of the relationships between energy, frequency, and wavelength ($E = h\nu = \frac{hc}{\lambda}$).

Thinking it Through: A photon is a packet of energy, the quantity of which is related to the frequency of the electromagnetic radiation. *Higher* frequencies (ν) and *shorter* wavelengths (λ) correlate with higher photon energies. All electromagnetic radiation travels at the velocity of light (c). The labels associated with regions of the electromagnetic spectrum are shown in the schematic diagram. Visible light and infrared radiation, choices **(C)** and **(D)**, are relatively low energy. Ultraviolet radiation, choice **(B)**, is higher in energy, but X-rays, choice **(A)**, are highest.

Electromagnetic Spectrum



AS-8. Which ground-state electron configuration is possible for an atom in the second period?

(A) $1s^2 2s^1 2p^1$ **(B)** $1s^2 2s^2 2d^1$ **(C)** $1s^2 2s^1$ **(D)** $1s^2 2p^4$

Knowledge Required: (1) The symbolic representation of electron configuration. (2) The meaning of the term "second period." (3) The allowed values for principal and angular momentum quantum numbers. (4) The order of filling of electron orbitals. (5) The ability to correlate symbolic representations with positions in the periodic table.

Thinking it Through: For the second period, the principal quantum number, n, is equal to 2. For a principal quantum number of 2, the angular momentum (shape) quantum number, l, has allowed values of 0 or 1. The letter s is associated with $l = 0$, and the letter p is associated with $l = 1$. Choice **(B)** cannot be correct, since only s and p orbitals are possible when $n = 2$. Choice **(D)** is eliminated because the $2s$ orbital must fill before the $2p$ orbital. The $2s$ orbital has room for two electrons, which must be occupied before the $2p$ orbital begins to fill. Choice **(A)** is eliminated because the order of filling is incorrect. Choice **(C)** has the correct orbitals present for a second period element, and also displays the correct order for filling orbitals. It is the electron configuration for lithium.

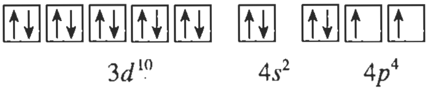
AS-9. The number of unpaired electrons in a gaseous selenium atom is

(A) 2 **(B)** 3 **(C)** 4 **(D)** 5

Knowledge Required: (1) Hund's rule. (2) The order of filling of electron orbitals. (3)The ability to correlate symbolic representations with positions in the periodic table.

Thinking it Through: Selenium is in Group VIA, the fourth column of the *p*-block. Lower energy orbitals are completely filled. Hund's rule specifies that electrons in orbitals of the same energy do not pair until they have to. Initially, there are three equal-energy *p* orbitals. The order of filling first places a single electron in each *p* orbital, and then forming one pair with the fourth electron. This leaves *two* electrons unpaired in equal-energy orbitals. Here is a symbolic representation of the same information.

Se $[Ar]^{18}\,3d^{10}4s^{2}4p^{4}$



Note: *Paramagnetism* is an experimental phenomena associated with atoms having unpaired electrons. Such substances are attracted to a magnetic field.

AS-10. Which electron transition in a hydrogen atom is associated with the largest *emission* of energy?

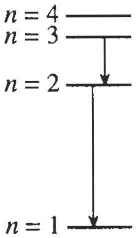
(A) $n = 2$ to $n = 1$ **(B)** $n = 2$ to $n = 3$

(C) $n = 2$ to $n = 4$ **(D)** $n = 3$ to $n = 2$

Knowledge Required: (1) The nature of quantized energy transfer between energy states. (2) The relative spacing of energy levels from $n = 1$ to $n = \infty$. (3) The interpretation of energy level changes.

Thinking it Through: Atomic line spectra provide evidence that the energy state of an electron in an atom is quantized. Only transitions between discrete energy states can take place.

Energy must be *absorbed* by the atom for an electron to move from one energy state in an atom to another energy state that is more remote from the nucleus. This observation eliminates both choices (**B**) and (**C**). The transitions in (**A**) and (**D**) both emit energy, and involve movement to the next lower energy state. Examining the relative spacing of energy levels reveals that $n = 2$ to $n = 1$ is the greater of the two.



Practice Questions

1. In all neutral atoms, there are equal numbers of

(A) protons and neutrons. **(B)** positrons and electrons.

(C) neutrons and electrons. **(D)** electrons and protons.

2. Which element is represented by $^{56}_{24}X$?

(A) iron **(B)** germanium **(C)** barium **(D)** chromium

3. Which statement concerning the structure of the atom is correct?

(A) Protons and neutrons have most of the mass and occupy most of the volume of the atom.

(B) Electrons have most of the mass and occupy most of the volume of the atom.

(C) Electrons have most of the mass but occupy very little of the volume of the atom.

(D) Protons and neutrons have most of the mass but occupy very little of the volume of the atom.

4. The number of neutrons in the $^{37}_{17}Cl^-$ ion is

(A) 17 **(B)** 20 **(C)** 21 **(D)** 37

5. An argon atom is isoelectronic with

(A) Cl **(B)** Ca **(C)** Ti^{4+} **(D)** N^{3-}

6. Which pair of particles has the same number of electrons?

(A) F^-, Mg^{2+} **(B)** Ne, Ar

(C) Br^-, Se **(D)** Al^{3+}, P^{3-}

7. Which ion has twenty-six electrons?

(A) Cr^{2+} **(B)** Fe^{2+} **(C)** Ni^{2+} **(D)** Cu^{2+}

8. Which statement is true?

(A) The nucleus of an atom contains neutrons and electrons.

(B) The atomic number of an element is the number of protons in one atom.

(C) The mass number of an atom is the number of protons in the nucleus plus the number of electrons outside.

(D) The number of electrons outside the nucleus is the same as the number of neutrons in the nucleus.

9. In what respect does an atom of magnesium, Mg, differ from a magnesium ion, Mg^{2+}?

(A) The ion has an inert gas electron configuration; the atom does not.

(B) The positive charge on the nucleus of the ion is two units greater than the nuclear charge on the atom.

(C) The ion has two more protons than the atom.

(D) The ion has two more planetary electrons than the atom.

10. A sodium ion differs from a sodium atom in that the sodium ion

(A) has fewer electrons.

(B) is an isotope of sodium.

(C) exists only in solution.

(D) has a negative charge on its nucleus.

11. Which term best characterizes the relation of hydrogen to deuterium?

(A) allotropes **(B)** isomers **(C)** isotopes **(D)** polymers

12. The element **X** occurs naturally to the extent of 20.0% ^{12}**X** and 80.0% ^{13}**X**. The atomic mass of **X** is nearest

(A) 12.2 **(B)** 12.5 **(C)** 12.8 **(D)** 13.0

13. In which pair are the two species ***both*** isoelectronic and isotopic?

(A) ${}^{40}_{20}\text{Ca}^{2+}$ and ${}^{40}_{18}\text{Ar}$ (B) ${}^{39}_{19}\text{K}^{+}$ and ${}^{40}_{19}\text{K}^{+}$

(C) ${}^{24}_{12}\text{Mg}^{2+}$ and ${}^{25}_{12}\text{Mg}$ (D) ${}^{56}_{26}\text{Fe}^{2+}$ and ${}^{57}_{26}\text{Fe}^{3+}$

14. An atom of the element of atomic number 84 and mass number 199 emits an alpha particle. The residual atom after this change has an atomic number of ____ and a mass number of _____.

(A) 82, 195 (B) 84, 203 (C) 85, 195 (D) 86, 199

15. In effecting nuclear changes by bombarding target nuclei with positively charged alpha particles, it is necessary to accelerate these particles to high speed because it is necessary to

(A) drive the positive particles through the electron cloud.

(B) overcome the force of repulsion of the nucleus.

(C) focus the bombarding particle more accurately.

(D) strip electrons from the atom.

16. What significant information about atomic structure came from the Millikan experiment using charged oil drops?

(A) Millikan showed that cathode rays were identical to a stream of electrons coming from an atom.

(B) Millikan confirmed that the neutron and proton were of about the same mass.

(C) Millikan determined the magnitude of the charge on an electron.

(D) Millikan proved that the mass of an atom was concentrated in the nucleus.

17. What is the valence electron configuration for the element in Period 5, Group 3A?

(A) $5s^25p^1$ (B) $3s^23p^5$ (C) $3s^23p^3$ (D) $5s^25p^3$

18. Which electron configuration is ***impossible***?

(A) $1s^22s^22p^63s^2$ (B) $1s^22s^22p^62d^2$

(C) $1s^22s^22p^63s^23p^6$ (D) $1s^22s^22p^53s^1$

19. The ground–state electronic configuration of the manganese atom, Mn, is

(A) $1s^22s^22p^63s^23p^64s^2\,4d^5$ (B) $1s^22s^22p^63s^23p^63d^7$

(C) $1s^22s^22p^63s^23p^64s^24p^5$ (D) $1s^22s^22p^63s^23p^63d^54s^2$

20. Which species has this ground-state electron arrangement?

$$1s^22s^22p^63s^23p^63d^{10}$$

(A) Ni (B) Ni^{2+} (C) Zn (D) Zn^{2+}

21. The maximum number of electrons that can occupy an orbital labeled d_{xy} is

(A) 1 (B) 2 (C) 3 (D) 4

22. An atom of Fe has two 4*s* electrons and six 3*d* electrons. How many ***unpaired*** electrons would there be in the Fe^{2+} ion?

(A) one **(B)** two **(C)** three **(D)** four

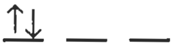
23. Which of these species (is/are) paramagnetic?

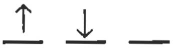
Ti^{4+} Fe^{2+} Zn^{o}

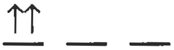
(A) Fe^{2+} only **(B)** Zn^{o} only

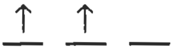
(C) Ti^{4+} and Fe^{2+} only **(D)** Fe^{2+} and Zn^{o} only

24. Which of these electron diagrams could represent the ground state of the *p* valence electrons of carbon?

(A) 

(B) 

(C) 

(D) 

25. The existence of discrete (quantized) energy levels in an atom may be inferred from

(A) experiments on the photoelectric effect.

(B) diffraction of electrons by crystals.

(C) X-ray diffraction by crystals.

(D) atomic line spectra.

26. Which emission line in the hydrogen spectrum occurs at the highest frequency?

(A) $n = 3 \rightarrow n = 1$ **(B)** $n = 4 \rightarrow n = 2$

(C) $n = 7 \rightarrow n = 5$ **(D)** $n = 10 \rightarrow n = 8$

27. Which set of quantum numbers is correct and consistent with $n = 4$?

(A) $l = 3$ $m_l = -3$ $m_s = +\frac{1}{2}$ **(B)** $l = 4$ $m_l = +2$ $m_s = -\frac{1}{2}$

(C) $l = 2$ $m_l = +3$ $m_s = +\frac{1}{2}$ **(D)** $l = 3$ $m_l = -3$ $m_s = +1$

28. When an atom of an electropositive atom becomes an ion it

(A) gains electrons. **(B)** becomes larger.

(C) emits an alpha particle. **(D)** does none of these.

29. The orbitals of 2*p* electrons are often represented as being

(A) elliptical. **(B)** tetrahedral.

(C) dumbbell shaped. **(D)** spherical.

30. Helium, ${}^{4}_{2}He$, has two electrons in the 1*s* orbital. When it becomes singly ionized, forming He^{+},

(A) its spectrum resembles that of the hydrogen spectrum.

(B) the remaining electron is easier to remove.

(C) the nuclear charge has decreased by one.

(D) it has lost one atomic mass unit.

Answers to Study Questions

1. A
2. C
3. B
4. D
5. C
6. D
7. A
8. C
9. A
10. A

Answers to Practice Questions

1. D
2. D
3. D
4. B
5. C
6. A
7. C
8. B
9. A
10. A
11. C
12. C
13. B
14. A
15. B
16. C
17. A
18. B
19. D
20. D
21. B
22. D
23. A
24. D
25. D
26. A
27. A
28. D
29. C
30. A

Molecular Structure and Bonding

Understanding molecular structure requires knowledge of the spatial arrangement of atoms in a molecule. The geometric arrangement of atoms in molecules can be determined by experiment, but bonding theories and properties such as dipole moment, which is a measure of molecular polarity, can help predict and rationalize molecular shape and chemical behavior. This section of most general chemistry courses deals with valence-shell electron-pair repulsion (VSEPR) models, prediction of bond angles, valence bond theory, hybrid orbitals, and molecular orbital theory.

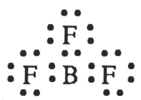
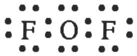
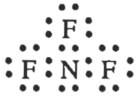
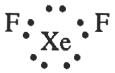
Study Questions

MS-1. Which molecule has exactly two unshared (lone) pairs of electrons on the central atom?

(A) BF_3 **(B)** OF_2 **(C)** NF_3 **(D)** XeF_2

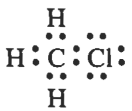
Knowledge Required: (1) The rules for drawing Lewis structures. (2) The exceptions to the octet rule.

Thinking it Through: Start by finding the total number of valence electrons that are available. The group number for the main group or representative (A group) elements gives this number. Fluorine, for example, is a member of Group VIIA and has 7 valence electrons. Distribute the electrons to satisfy the octet rule, keeping in mind the common exceptions.

BF_3	3 + 3(7) = 24 valence electrons		No unshared pairs on boron.
OF_2	6 + 2(7) = 20 valence electrons		Exactly two unshared pairs on oxygen.
NF_3	5 + 3(7) = 26 valence electrons		One unshared pair on nitrogen.
XeF_2	8 + 2(7) = 22 valence electrons		Three unshared pairs on xenon.

Note that there are two common exceptions here. Boron has too few valence electrons to form a full octet, and xenon can form an expanded octet, making both choices **(A)** and **(D)** incorrect. NF_3 has only one lone pair, so choice **(C)** is also incorrect. Only OF_2 has exactly two unshared pairs of electrons on the central atom, making choice **(B)** the correct answer.

MS-2. Consider the Lewis structure for CH_3Cl. What is the best description of the molecular shape?



(A) bent

(B) square

(C) square pyramidal

(D) tetrahedral

Knowledge Required: (1) The interpretation of Lewis structures. (2) The valence-shell-electron-pair-repulsion (VSEPR) model for predicting molecular shape.

Thinking it Through: The first step in applying the VSEPR method is to count the number of electron regions around the central atom. In this case, the Lewis structure is given, showing four pairs of electrons around the carbon atom. These electron pairs are all used to form bonds, and there are no lone pairs. Electron pair repulsion is minimized when the four electron pairs form a tetrahedron around the carbon atom, choice **(D)**. Observe the similarity to methane, CH_4, which was probably the first tetrahedral molecule you studied.
Note: In other questions you may be asked about the *tetrahedral bond angle*, which is 109.5°.

MS-3. The fact that BCl_3 is a planar molecule while NCl_3 is pyramidal can be explained several different ways. Which statement is the best rationalization?

(A) Nitrogen is more electronegative than boron.

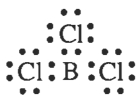
(B) The nitrogen atom in NCl_3 has a lone pair of electrons, whereas the boron atom in BCl_3 does not.

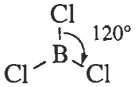
(C) The nitrogen atom is smaller than the boron atom.

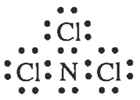
(D) The boron atom in BCl_3 is sp^3 hybridized, while the nitrogen atom in NCl_3 is sp^2 hybridized.

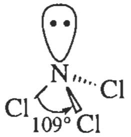
Knowledge Required: (1) The valence-shell-electron-pair-repulsion (VSEPR) model for predicting molecular shape. (2) The valence-bond theory for predicting hybridization of orbitals.

Thinking it Through: Choices **(A)** and **(C)** are both true statements, but neither provides the *reason* for the difference in geometries. The VSEPR model does provide a rationalization for the difference. Choice **(D)** has the hybridization reversed. NCl_3 has an sp^3 hybridized nitrogen atom, and BCl_3 has an sp^2 hybridized boron atom. Choice **(B)**, the correct answer, recognizes that boron has only enough valence electrons to form three bonds, with no lone pairs. The six electrons arrange themselves to have 120° Cl–B–Cl bond angles. On the other hand, when NCl_3 forms three bonds it has an electron pair left over to complete the octet. The four electron pairs arrange themselves in the shape of a tetrahedron around the nitrogen atom. Here are the Lewis structures and their three-dimensional representations:









MS-4. According to the VSEPR model, the geometric structure of H_2O is

(A) bent at an angle of 104.5° because of the greater repulsion of two lone pairs relative to that of the two bonding pairs.

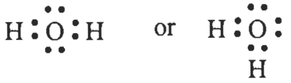
(B) bent at an angle of 120° because of the mutual repulsion of the six valence electrons on oxygen.

(C) bent at an angle of 90° because of the perpendicular relationship of the oxygen *p* orbitals relative to each other.

(D) linear with a bond angle of 180° because of the mutual repulsion of the bonding pairs of electrons.

Knowledge Required: (1) Valence-shell-electron-pair-repulsion (VSEPR) model for predicting molecular shape. (2) Effect of lone pairs on predicted bond angles.

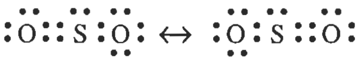
Thinking it Through: Recall or write the Lewis structure for the water molecule.



$$H:\underset{..}{\overset{..}{O}}:H \quad \text{or} \quad H:\underset{\underset{H}{..}}{\overset{..}{O}}:$$

A Lewis structure by itself does not provide information about geometry. Use VSEPR to predict geometry by counting bonded and nonbonded electron pairs. If there are four bonded pairs to identical atoms, the exact tetrahedral angle of 109.5° can be expected. That is the case with CH_4. In NH_3 there are three bonded pairs and one nonbonded pair, so the bond angle closes slightly (to 107°) as the result of the lone pair requiring more space than the bonded pairs. In the water molecule, with two nonbonded pairs, the H–O–H bond angle closes to 104.5° because of repulsion from the lone pairs. **(A)** is the correct choice. Choice **(B)** has the bond angle larger, rather than smaller, than the tetrahedral angle. Choice **(C)** treats the orbitals as if they had the geometry of atomic orbitals. Choice **(D)** fails to recognize the three-dimensional nature of molecules.

MS-5. Sulfur dioxide can be described by the structures shown. This symbolism indicates that the



$$:\overset{..}{O}::\overset{..}{S}:\underset{..}{\overset{..}{O}}: \leftrightarrow :\underset{..}{\overset{..}{O}}:\overset{..}{S}::\overset{..}{O}:$$

(A) two bonds in SO_2 are of equal length, and the electronic distribution in the two sulfur-to-oxygen bonds is identical.

(B) single bond is longer than the double bond, and the electronic distribution in the two sulfur-to-oxygen bonds differs.

(C) electron pair in the SO_2 molecule alternates back and forth between the two sulfur-oxygen electron pairs, so that the two different bonds seem to exchange positions.

(D) SO_2 molecule revolves, so that the two different sulfur-to-oxygen bonds seem to exchange positions.

Knowledge Required: (1) The meaning of resonance structures. (2) The interpretation of Lewis structures.

Thinking it Through: A single Lewis electron-dot formula cannot always adequately describe bonding between atoms. If two (or more) formulas satisfy the octet rule, the Lewis structures are both written and resonance is indicated with a double-headed arrow. This does *not* mean that the molecule oscillates between the structures. Rather, it means that the actual structure is intermediate between (or among) the resonance forms. Choices **(C)** and **(D)** suggest movement of electrons or atoms, which does not occur. Choice **(B)** suggests that the sulfur–oxygen bonds are not equivalent, but they are. Correct choice **(A)** recognizes that the two bonds are identical. The need to draw two forms reflects a limitation of the Lewis-dot model.

MS-6. A compound consisting of an element having a low ionization energy and a second element having a high electron affinity is likely to have

(A) covalent bonds.

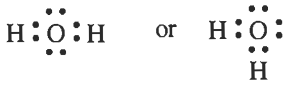
(B) metallic bonds.

(C) coordinate covalent bonds.

(D) ionic bonds.

Knowledge Required: (1) Valence-shell-electron-pair-repulsion (VSEPR) model for predicting molecular shape. (2) Effect of lone pairs on predicted bond angles.

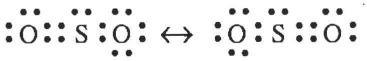
Thinking it Through: Recall or write the Lewis structure for the water molecule.



$$\mathrm{H}:\overset{..}{\underset{..}{\mathrm{O}}}:\mathrm{H} \quad \text{or} \quad \mathrm{H}:\overset{..}{\underset{\underset{\mathrm{H}}{..}}{\mathrm{O}}}:$$

A Lewis structure by itself does not provide information about geometry. Use VSEPR to predict geometry by counting bonded and nonbonded electron pairs. If there are four bonded pairs to identical atoms, the exact tetrahedral angle of 109.5° can be expected. That is the case with CH_4. In NH_3 there are three bonded pairs and one nonbonded pair, so the bond angle closes slightly (to 107°) as the result of the lone pair requiring more space than the bonded pairs. In the water molecule, with two nonbonded pairs, the H–O–H bond angle closes to 104.5° because of repulsion from the lone pairs. (**A**) is the correct choice. Choice (**B**) has the bond angle larger, rather than smaller, than the tetrahedral angle. Choice (**C**) treats the orbitals as if they had the geometry of atomic orbitals. Choice (**D**) fails to recognize the three-dimensional nature of molecules.

MS-5. Sulfur dioxide can be described by the structures shown. This symbolism indicates that the



$$:\overset{..}{\mathrm{O}}::\overset{..}{\mathrm{S}}:\overset{..}{\underset{..}{\mathrm{O}}}: \leftrightarrow :\overset{..}{\underset{..}{\mathrm{O}}}:\overset{..}{\mathrm{S}}::\overset{..}{\mathrm{O}}:$$

(A) two bonds in SO_2 are of equal length, and the electronic distribution in the two sulfur-to-oxygen bonds is identical.

(B) single bond is longer than the double bond, and the electronic distribution in the two sulfur-to-oxygen bonds differs.

(C) electron pair in the SO_2 molecule alternates back and forth between the two sulfur-oxygen electron pairs, so that the two different bonds seem to exchange positions.

(D) SO_2 molecule revolves, so that the two different sulfur-to-oxygen bonds seem to exchange positions.

Knowledge Required: (1) The meaning of resonance structures. (2) The interpretation of Lewis structures.

Thinking it Through: A single Lewis electron-dot formula cannot always adequately describe bonding between atoms. If two (or more) formulas satisfy the octet rule, the Lewis structures are both written and resonance is indicated with a double-headed arrow. This does *not* mean that the molecule oscillates between the structures. Rather, it means that the actual structure is intermediate between (or among) the resonance forms. Choices (**C**) and (**D**) suggest movement of electrons or atoms, which does not occur. Choice (**B**) suggests that the sulfur–oxygen bonds are not equivalent, but they are. Correct choice (**A**) recognizes that the two bonds are identical. The need to draw two forms reflects a limitation of the Lewis-dot model.

MS-6. A compound consisting of an element having a low ionization energy and a second element having a high electron affinity is likely to have

(A) covalent bonds.

(B) metallic bonds.

(C) coordinate covalent bonds.

(D) ionic bonds.

Knowledge Required: (1) The meaning of the terms ionization energy and electron affinity. (2) The characteristics of different types of chemical bonds. (3) The relationship between types of chemical bonds and values of ionization energy and electron affinity.

Thinking it Through: Elements with low ionization energy readily lose electrons to form positive ions. Elements with high electron affinity readily accept electrons to form negative ions. Ionic bonds, correct choice (**D**), result when atoms exchange electrons. Covalent bonds, choice (**A**), result when atoms each contribute an electron to a shared pair. Coordinate covalent bonds, choice (**C**), are similar except one of the two atoms furnishes both electrons. Metallic bonds, choice (**B**), result when atoms free one or more valence electrons to the metal lattice.

MS-7. The compound CF_3CHClF is being considered as a replacement for $CBrF_3$ as a fire-extinguishing agent because $CBrF_3$ has been shown to deplete stratospheric ozone. What are the most probable products if a molecule of CF_3CHClF is bombarded with high-energy photons?

Bond	Bond Energy, $kJ \cdot mol^{-1}$
C–C	346
C–Cl	327
C–F	485
C–H	411

(A) $CF_3 + CHClF$

(B) $CF_2CHClF + F$

(C) $CF_3CHF + Cl$

(D) $CF_3CClF + H$

Knowledge Required: (1) The knowledge of the interaction of photons with covalent bonds. (2) The interpretation of bond energy data.

Thinking it Through: High-energy photons, such as those in the ultraviolet part of the electromagnetic spectrum, have enough energy to disrupt covalent bonds. In choosing from the set of possible products resulting from breaking at least one covalent bond, it may be helpful to consider the Lewis structure. Choice (**A**) requires breaking the C–C bond, which would require 346 kJ per mol. Choice (**B**) requires breaking one of the C–F bonds, but that would require 485 kJ per mol. The correct choice (C) results from breaking a C–Cl bond, the bond requiring the least energy of the choices given, 327 kJ per mol. Choice (**D**) could result if a C–H bond were broken, but that is less favorable at 411 kJ per mol. Note: Halon compounds contain bromine covalently bonded to carbon. This bond is even more easily broken by high-energy photons. The C–Br bond energy is 285 $kJ \cdot mol^{-1}$.

MS-8. A simple method of showing experimentally that a solid substance may be ionic is to show that it

(A) has a high melting point.

(B) is soluble in polar solvents.

(C) depresses the freezing point of water.

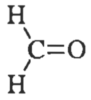
(D) conducts current when dissolved in water.

Knowledge Required: (1) The nature of ionic bonding and properties of ionic compounds. (2) The attributes of solutions of ionic compounds in water.

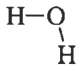
Thinking it Through: Choice (**A**) could be true, but melting point is not a valid criterion for establishing the presence of ionic bonds. Several covalent network solids have melting points of several thousand degrees Celsius. Choice (**B**) is true for ionic compounds, as it is for polar covalent compounds that do not react with water to form ions. Alcohols, for example, are miscible with water, but they are not ionic compounds. Choice (**C**) is true for both ionic and covalent compounds. In fact, *any* nonvolatile solute that is dissolved in water depresses its freezing point. Ethylene glycol, a covalent compound, is used as antifreeze in automobile radiators. Choice (**D**) is true only for ionic compounds. (Some liquid and gaseous covalent compounds react with water to form ions; hence, the necessity of including the word "solid" in the stem.)

MS-9. Which of these is a nonpolar molecule?

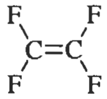
(A)



(B)



(C)



(D) I–Br

Knowledge Required: (1) The relative electronegativity of atoms. (2) The properties of polar bonds. (3) The molecular geometry of molecules. (4) The relationship of dipole moment to molecular geometry.

Thinking it Through: For a molecule to be nonpolar when it has polar bonds, it must be symmetric enough that all the bond dipoles cancel each other out. For choice **(A)**, the pull of the oxygen on the electrons shared with carbon is not cancelled from the other side, and the molecule is polar. The same is true for choices **(B)** and **(D)**. Choice **(C)** contains polar carbon-fluorine bonds, with the polarity of each one cancelled by a carbon–fluorine bond on the opposite side of the molecule.

MS-10. For which molecule can the bonding be described in terms of sp^3 hybrid orbitals of the central atom?

(A) SF_6 **(B)** BF_3 **(C)** PCl_5 **(D)** NH_3

Knowledge Required: (1) Geometry of hybrid orbitals. (2) Number of valence electrons for several atoms.

Thinking it Through: To form sp^3 hybrid orbitals, valence-bond theory uses one *s* orbital and three *p* orbitals to produce four equivalent orbitals oriented toward the corners of a tetrahedron. Each of the hybrid orbitals has a capacity of two electrons, for a maximum of eight electrons in the valence shell. When sulfur forms two-electron bonds with each of six fluorine atoms, as in choice **(A)**, the sulfur must form a hybrid that uses *six* atomic orbitals rather than four. Similarly, the phosphorus atom in choice **(C)** must form hybrids that use *five* atomic orbitals. Boron, with only three valence electrons, cannot place one in each of four hybrid orbitals. It is only able to form sp^2 hybrid orbitals, except when a bonding partner provides both of the share electrons. Boron is a sp^2 hybrid in BF_3, choice **(B)**. A nitrogen atom, with five valence electrons, forms bonds with three hydrogen atoms. There are eight valence electrons, enough to fill four sp^3 hybrid orbitals, choice **(D)**.

Practice Questions

1. NH_3 (pyramidal geometry) reacts with BF_3 (planar geometry) to form the addition compound, H_3NBF_3. What is the geometry around the nitrogen and boron centers in the addition compound?

(A) Both centers are tetrahedral.
(B) Nitrogen is tetrahedral; boron is linear.
(C) Nitrogen is pyramidal; boron is planar.
(D) Nitrogen is planar; boron is pyramidal.

2. The molecule of the type $\mathbf{ML_4}$ consists of four single bonds and no lone pairs. What structure is it expected to assume?

(A) square planar
(B) trigonal planar
(C) trigonal pyramidal
(D) tetrahedral

3. The shape that most closely describes the NF_3 molecule is

(A) octahedral.
(B) trigonal planar.
(C) trigonal pyramidal.
(D) tetrahedral.

4. In which pair are the molecules geometrically similar?

(A) SO_2 and CO_2
(B) PH_3 and BF_3
(C) CO_2 and OF_2
(D) SO_2 and O_3

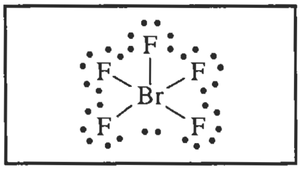
5. Which is planar?

(A) NH_3 **(B)** SO_3^{2-} **(C)** CO_3^{2-} **(D)** CCl_4

6. Which is linear?

(A) H_2S **(B)** NH_3 **(C)** NO_2 **(D)** CO_2

7. Consider the given Lewis structure for BrF_5. What is the predicted shape for the molecule as a whole?



(A) square pyramidal
(B) trigonal bipyramidal
(C) trigonal pyramidal
(D) octahedral

8. What is the shape of the XeF_4 molecule?

(A) square planar
(B) trigonal bipyramidal
(C) tetrahedral
(D) trigonal pyramidal

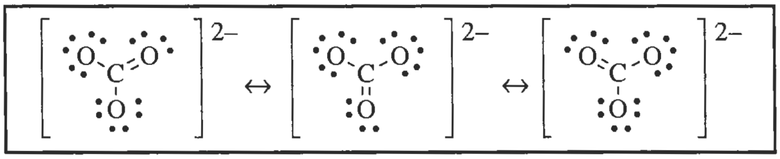
9. What set of species is arranged in order of increasing O–N–O bond angle?

(A) NO_2^-, NO_2, NO_2^+
(B) NO_2, NO_2^-, NO_2^+
(C) NO_2^+, NO_2, NO_2^-
(D) NO_2, NO_2^+, NO_2^-

10. Which has the largest bond angle?

(A) angle O–S–O in SO_4^{2-}
(B) angle Cl–C–Cl in $HCCl_3$
(C) angle F–Be–F in BeF_2
(D) angle H–O–H in H_2O

11. The structure of the CO_3^{2-} ion can be described in the Lewis formulation by these structures. This means that



(A) two carbon-to-oxygen bonds are single bonds; the third is a double bond.
(B) three independent forms of the CO_3^{2-} ion coexist in equilibrium.
(C) the electrons must be rapidly exchanging among the three forms.
(D) the CO_3^{2-} ion exists in only one form: an average of the three principal structures shown.

12. Which concept describes the formation of four equivalent, single, covalent bonds by carbon in its compounds that resemble methane, CH_4?

(A) hydrogen bonding **(B)** hybridization

(C) sigma bonding **(D)** coordinate covalent bonding

13. Which type of hybrid orbital is used in CO_2?

(A) *sp* **(B)** sp^2 **(C)** sp^3 **(D)** dsp^3

14. Which compound would be expected to have the largest dipole moment?

(A) CO_2 (linear) **(B)** SO_2 (bent)

(C) BF_3 (trigonal planar) **(D)** CF_4 (tetrahedral)

15. The O–Si–O bond angles in SiO_2 (quartz) are closest to

(A) 180° **(B)** 120°

(C) 110° **(D)** 100°

16. The molecule $:\ddot{O}=C=\ddot{N}-H$ has been detected in gas clouds between stars. The predicted C–N–H bond angle is about

(A) 90° **(B)** 109° **(C)** 120° **(D)** 180°

17. Knowing that F is more electronegative than either B or P, what conclusion can be drawn from the fact that BF_3 has no dipole moment, but PF_3 does?

(A) BF_3 is not spherically symmetrical, but PF_3 is.

(B) The BF_3 molecule must be trigonal planar.

(C) The BF_3 molecule must be linear.

(D) The atomic radius of P is larger than the atomic radius of B.

18. How many valence electrons are represented in the Lewis electron-dot structure for SO_2?

(A) 6 **(B)** 8 **(C)** 18 **(D)** 32

19. Molecules of which compounds violate the octet rule?

NO_2	CH_2Cl_2	XeF_4	NCl_3
1	**2**	**3**	**4**

(A) **1 and 2** **(B)** **1 and 3** **(C)** **2 and 3** **(D)** **2 and 4**

20. The boiling point of H_2O, compared with the other members of the series, can be explained by

Boiling Points of Group VIA Hydrides

H_2O	H_2S	H_2Se	H_2Te
100 °C	–61 °C	–45 °C	–2 °C

(A) London dispersion forces. **(B)** dipole—induced dipole forces.

(C) hydrogen bonding. **(D)** nonpolar covalent bonding.

21. The fact that $Pt(NH_3)_2Cl_2$ exists in two different isomeric forms offers evidence that the geometry is

(A) octahedral.
(B) square planar.
(C) tetrahedral.
(D) trigonal planar.

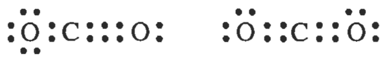
22. Which species has ***both*** covalent and ionic bonds?

(A) NH_3BF_3
(B) H_3O^+
(C) NaKS
(D) $Mg(CN)_2$

23. When the carbon–carbon bonds in ethane (C_2H_6), ethene (C_2H_4), and benzene (C_6H_6), are arranged in order of increasing length (shortest bonds first), what is the correct order?

(A) $C_2H_6 < C_2H_4 < C_6H_6$
(B) $C_2H_4 < C_2H_6 < C_6H_6$
(C) $C_6H_6 < C_2H_4 < C_2H_6$
(D) $C_2H_4 < C_6H_6 < C_2H_6$

24. These two electron-dot formulas for carbon dioxide both satisfy the octet rule, but one is preferred over the other. Which of the statements identifies the preferred structure and also the reason it is preferred?



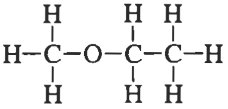
Structure **1** Structure **2**

(A) Structure **1** is preferred because the triple bond is stronger than the double bond.
(B) Structure **1** is preferred because the formal charge on carbon is negative.
(C) Structure **2** is preferred because the formal charge on each atom is zero.
(D) Structure **2** is preferred because the bonds are equal.

25. Which element is most likely to form a triple bond?

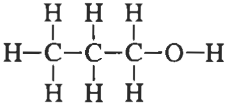
(A) Pb
(B) F
(C) N
(D) S

26. Which is an isomer of



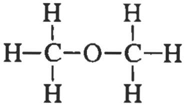
$H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$?

(A)



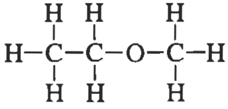
$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$

(B)



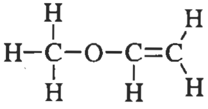
$H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-H$

(C)



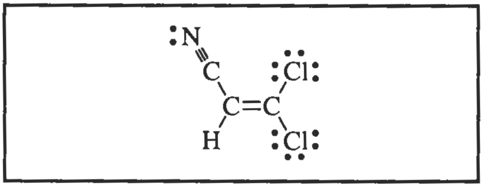
$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-H$

(D)



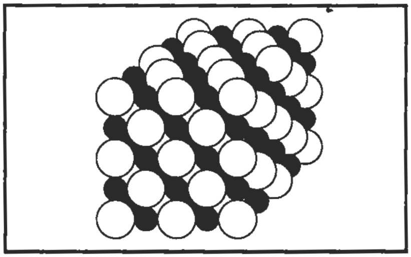
$H-\underset{H}{\overset{H}{C}}-O-\underset{H}{C}=C\begin{smallmatrix}H\\H\end{smallmatrix}$

27. How many sigma bonds and how many pi bonds are represented in this structure?



	Sigma Bonds	Pi Bonds
(A)	6	3
(B)	7	2
(C)	8	1
(D)	9	0

28. Sodium chloride, NaCl, crystallizes in a face-centered cubic lattice of chloride ions, with the smaller sodium ions occupying holes between the chloride ions. How many Cl^- ions are in contact with any single Na^+ ion?



(A) 4 (B) 6 (C) 8 (D) 12

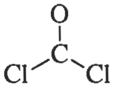
29. Resonance structures describe molecules that have

(A) hybrid orbitals.

(B) rapid equilibria.

(C) resonating electrons.

(D) multiple electron-dot formulas.

30. The complete Lewis structure of  will have

(A) at least one lone pair on each atom.

(B) at least one double bond.

(C) both polar and nonpolar bonds.

(D) resonance forms.

Answers to Study Questions

1. B
2. D
3. B
4. A
5. A
6. D
7. C
8. D
9. C
10. D

Answers to Practice Questions

1. A
2. D
3. C
4. D
5. C
6. D
7. A
8. A
9. A
10. C
11. D
12. B
13. A
14. B
15. C
16. C
17. B
18. C
19. B
20. C
21. B
22. D
23. D
24. C
25. C
26. A
27. A
28. B
29. D
30. B

Stoichiometry

Chemical stoichiometry is the area of study that considers the quantities of materials in chemical formulas and equations. Quite simply, it is chemical arithmetic. The word itself is derived from *stoicheion*, the Greek word for element and *metron*, the Greek word for measure. When based on chemical formulas, stoichiometry is used to convert between mass and moles, to calculate the number of atoms, to calculate percent composition, and to interpret the mole ratios expressed in a chemical formula. Most topics in chemical arithmetic depend on the interpretation of balanced chemical equations. Mass/mole conversions, calculation of limiting reagent and percent yield, and various relationships among reactants and products are commonly included in this topic area.

Study Questions

ST-1. What is the empirical formula for the substance with this analysis?

Elemental Analysis by Mass	
Na	54.0%
B	8.50%
O	37.5%

(A) Na_3BO_3 **(B)** $Na_2B_2O_3$ **(C)** Na_4BO_4 **(D)** $Na_3B_2O_2$

Knowledge Required: (1) The meaning of empirical formula. (2) The interpretation of elemental analysis data.

Thinking it Through: An empirical formula is also called the simplest formula. Both terms refer to the lowest whole number ratios of atoms in a molecule or formula unit, and are derived from experiments. Such experiments yield the relative percentage of elements in a compound, expressed as percentage by mass. Formulas give the mole ratio of each element in the compound, so the first step is to convert each mass percentage to a relative mole value. It is easiest to do by assuming 100 g of the compound. Therefore, in each 100 grams of this compound there will be 54.0 g of sodium, 8.50 g of boron, and 37.5 g of oxygen. The molar mass of each element is used to find the number of moles.

$$54.0\text{ g Na}\times\frac{1\text{ mol Na}}{23.0\text{ g Na}}=2.35\text{ mol Na}\qquad 8.50\text{ g B}\times\frac{1\text{ mol B}}{10.8\text{ g B}}=0.787\text{ mol B}\qquad 37.5\text{ g O}\times\frac{1\text{ mol O}}{16.0\text{ g O}}=2.34\text{ mol O}$$

These values correctly represent the ratio of sodium, boron, and oxygen atoms in the compound, but it is not the usual practice to write formulas such as $Na_{2.35}B_{0.787}O_{2.34}$. To find the ratio of whole numbers needed for the formula, divide each value by the smallest number of moles. In this case, the smallest number of moles is 0.787 mol B.

$$\frac{2.35\text{ mol Na}}{0.787\text{ mol B}}=\frac{2.99\text{ mol Na}}{1.00\text{ mol B}}\approx\frac{3\text{ mol Na}}{1\text{ mol B}}\qquad\frac{2.34\text{ mol O}}{0.787\text{ mol B}}=\frac{2.97\text{ mol O}}{1.00\text{ mol B}}\approx\frac{3\text{ mol O}}{1\text{ mol B}}$$

This whole number ratio shows that the correct formula is Na_3BO_3, which is choice **(A)**.

Note: The percent composition values are experimental values, so do not expect the mole ratios to be *exactly* whole number ratios. However, if the mole ratios are more than one or two percent from whole numbers after the second step, consider multiplying through each ratio by a small integer to convert to whole numbers. See practice problem 2 for an example of this.

ST-2. What is the mass percent of oxygen in $Fe_2(SO_4)_3$?

Atomic Molar Mass Data	
Fe	55.85 g·mol^{-1}
S	32.06 g·mol^{-1}
O	16.00 g·mol^{-1}

(A) 15.40% **(B)** 18.76% **(C)** 30.80% **(D)** 48.01%

Knowledge Required: (1) The meaning of mass percent. (2) The interpretation of chemical formulas.

Thinking it Through: This type of question starts with a chemical formula and uses it to determine the mass percent for any element in a compound. Mass percent is a comparison of the mass of the element being considered to the molar mass of the compound. The ratio is then multiplied by 100 to make it a percent, which is the same as parts per hundred. In this case, the mass of oxygen present must be compared to the molar mass of the compound, $Fe_2(SO_4)_3$.

$$\%\,\mathrm{O} = \frac{\left(12\text{ mol O } \times \dfrac{16.00\text{ g}}{1\text{ mol O}}\right)}{\left(2\text{ mol Fe} \times \dfrac{55.85\text{ g}}{1\text{ mol Fe}}\right) + \left(3\text{ mol S} \times \dfrac{32.06\text{ g}}{1\text{ mol S}}\right) + \left(12\text{ mol O} \times \dfrac{16.00\text{ g}}{\text{mol O}}\right)} \times 100$$

$$\%\,\mathrm{O} = \frac{192.0\text{ g O}}{399.88\text{ g Fe}_2(\mathrm{SO}_4)_3} \times 100$$

$$\%\,\mathrm{O} = 48.01\%\text{ O by mass}$$

This is choice **(D)**. Errors arise if the formula is misinterpreted and an incorrect number of atoms are counted, leading to an incorrect value for either the mass of oxygen or the mass of the total compound.

Mass percent questions are often part of a practical application, such as choosing an ore with the highest percentage of the metal desired or choosing a hydrocarbon fuel with the highest percentage of carbon. Note also that if a mass percent is given, it would be possible to work back to determine the mass of an element or a group of elements within a compound.

ST-3. A typical silicon chip, such as those in electronic calculators, has a mass of 2.3×10^{-4} g. Assuming the chip is pure silicon, how many silicon atoms are in such a chip?

(A) 4.9×10^{18} **(B)** 1.4×10^{20} **(C)** 3.9×10^{21} **(D)** 2.6×10^{27}

Knowledge Required: (1) The method for carrying out mass to mole conversions. (2) The application of Avogadro's number.

Thinking it Through: Avogadro's number, 6.02×10^{23}, gives the number of silicon atoms in each mole of silicon. This means that calculating the number of moles of silicon present is an essential first step before using Avogadro's number to find the number of silicon atoms.

$$2.3 \times 10^{-4}\text{ g} \times \frac{1\text{ mol Si}}{28\text{ g Si}} \times \frac{6.02 \times 10^{23}\text{ atoms Si}}{1\text{ mol Si}} = 4.9 \times 10^{18}\text{ atoms Si}$$

Note the two factors used to make the conversion from grams of silicon to atoms. The first factor is the molar mass of silicon. Such values will always be available to you from the periodic table that accompanies all ACS exams. The value of Avogadro's number will also be given in a table of useful information; or, sometimes it is included with the question itself. Since you use this value so often, you probably already know it. These two conversion factors are arranged so that the units cancel in making the change from grams through moles to atoms. If the conversion were desired in the reverse direction, then both factors would be inverted.

ST-4. A hydrocarbon with general formula C_xH_y was burned completely in air, yielding 0.18 g of water and 0.44 g of carbon dioxide. Which formula could give such data?

Formula	Molar Mass
H_2O	$18.0\ \mathrm{g{\cdot}mol^{-1}}$
CO_2	$44.0\ \mathrm{g{\cdot}mol^{-1}}$

(A) C_2H_2 **(B)** C_2H_4 **(C)** C_2H_6 **(D)** C_6H_6

Knowledge Required: (1) The expected products of combustion reactions of hydrocarbons. (2) The interpretation of experimental data. (3) The determination of mole ratio in a formula.

Thinking it Through: This is the general equation for the complete combustion of a hydrocarbon.

$$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + y/2H_2O$$

What is needed in this problem is the mole ratio of carbon to hydrogen in the hydrocarbon. The given masses of the products of complete combustion, water, and carbon dioxide, can be used to determine the needed mole ratio. By inspection, it can be seen that 0.44 g of CO_2 ($M = 44.0\ g{\cdot}mol^{-1}$) is 0.010 mol of CO_2. Similarly, in 0.18 g of H_2O ($M = 18.0\ g{\cdot}mol^{-1}$), there are 0.010 mol of H_2O.

Note: In this problem there has been an attempt to simplify the number for you to save unnecessary calculation. If the shortcut is not clear to you, you can always do the formal calculation.

$$0.44\ g\ CO_2 \times \frac{1\ mol\ CO_2}{44.0\ g\ CO_2} = 0.010\ mol\ CO_2 \qquad 0.18\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.0\ g\ H_2O} = 0.010\ mol\ H_2O$$

All of the carbon in the product carbon dioxide came from the original hydrocarbon; this means there is 0.010 mol C in C_xH_y. All of the hydrogen in the product water also came from the original hydrocarbon. The formula shows that there are two moles of hydrogen atoms in every mole of water molecules, so there are 0.010 mol of H in C_xH_y. Putting these observations together, there are twice the number of moles of hydrogen as carbon, fixing the formula as C_2H_4 which is choice (**B**).

The most common error in this type of problem is overlooking important subscripts, such as the "2" in the formula for water. If you make this error, however, you should be able to recover in this case, for there are two choices, both C_2H_2 and C_6H_6, that have a one-to-one mole ratio of carbon to hydrogen. Since there is no further information given that would enable you to differentiate between these two responses, you are alerted to check for an error.

ST-5. Calculate the mass of SbF_3 needed to produce 1.00 g of Freon–12, CCl_2F_2. The reaction is represented by this equation.

$$3CCl_4 + 2SbF_3 \rightarrow 3CCl_2F_2 + 2SbCl_3$$

Formula	Molar Mass
SbF_3	$179\ g{\cdot}mol^{-1}$
CCl_2F_2	$121\ g{\cdot}mol^{-1}$

(A) 0.667 g (B) 0.986 g (C) 1.48 g (D) 2.22 g

Knowledge Required: (1) The method for carrying out mass to mole conversions. (2) The interpretation of a balanced chemical equation.

Thinking it Through: The coefficients in a balanced chemical equation give the relative number of moles of each reactant and product. The first step is to change 1.00 g of CCl_2F_2 to moles of CCl_2F_2, using the given molar mass. An inspection of the coefficients in the balanced equation reveals that two moles of SbF_3 are needed to produce every three moles of CCl_2F_2. The last step is to use the molar mass of SbF_3 to change the moles of SbF_3 to grams of SbF_3. Here is the mathematical solution.

$$1.00\ g\ CCl_2F_2 \times \frac{1\ mol\ CCl_2F_2}{121\ g\ CCl_2F_2} \times \frac{2\ mol\ SbF_3}{3\ mol\ CCl_2F_2} \times \frac{179\ g\ SbF_3}{1\ mol\ SbF_3} = 0.986\ g\ SbF_3$$

The correct answer is in choice (**B**). You should realize that other possible answers have been carefully crafted to detect likely errors in solving this problem. For example, if you neglect the 2:3 mole ratio from the balanced equation, you will incorrectly calculate the mass of SbF_3 required to be 1.48 grams, choice (**A**). If you neglect to change grams to moles, but apply the mole ratio correctly, you will calculate the mass of SbF_3 required as 0.667 g; this is also wrong but it is choice (**A**). If the mole ratio is inverted in error, you will think 2.22 g is the correct answer, choice (**D**).

ST-6. What volume of 0.100 M $SO_3^{2-}(aq)$ is needed to titrate 24.0 mL of 0.200 M $Fe^{3+}(aq)$? This equation represents the reaction that takes place during the titration.

$$2Fe^{3+}(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2Fe^{2+}(aq) + SO_4^{2-}(aq) + 2H^+(aq)$$

(A) 48.0 mL **(B)** 24.0 mL **(C)** 12.0 mL **(D)** 6.00 mL

Knowledge Required: (1) The definition of molarity, M. (2) The interpretation of a balanced chemical equation.

Thinking it Through: Often chemical arithmetic is based not on a mass measurement, but on a volume measurement. The molarity of a solution expresses the number of moles of solute in a liter of solution. It is straightforward in this case to predict the volume of $SO_3^{2-}(aq)$ that will be required. The $SO_3^{2-}(aq)$ is *half* as concentrated as the $Fe^{3+}(aq)$ solution, but only *half* the number of moles are required according to the balanced equation. Therefore, 24.0 mL of the $SO_3^{2-}(aq)$ will be required for the titration to be completed. This is choice (**B**).

You may need the full mathematical solution in other cases where the numbers are not so simple. It is equally correct and often more convenient for laboratory work to interpret molarity as the number of millimoles of solute in a milliliter of solution; the ratio of solute to solution remains constant. The coefficients in the balanced ionic equation give the relative number of moles of each reactant and product; this ratio can also be expressed in millimoles.

$$24.0\text{ mL } Fe^{3+}(aq) \times \frac{0.200\text{ mmol } Fe^{3+}(aq)}{1\text{ mL } Fe^{3+}(aq)} \times \frac{1\text{ mmol } SO_3^{2-}(aq)}{2\text{ mmol } Fe^{3+}(aq)} \times \frac{1\text{ mL } SO_3^{2-}(aq)}{0.100\text{ mmol } SO_3^{2-}(aq)} = 24.0\text{ mL } SO_3^{2-}(aq)$$

Note that if you omit the 1:2 ratio of $SO_3^{2-}(aq)$ to $2Fe^{3+}(aq)$, you will erroneously calculate choice (**A**). Choices (**C**) and (**D**) do not meet a standard of reasonableness. It cannot possibly take *less* than 24.0 mL of 0.100 M $SO_3^{2-}(aq)$ to react with 24.0 mL of the more concentrated $Fe^{3+}(aq)$.

ST-7. If a 17.0 g sample of impure nickel metal reacts with excess carbon monoxide, CO, forming 6.25 L of $Ni(CO)_4$ gas under standard temperature and pressure conditions, what is the percent by mass of nickel in the impure nickel metal sample?

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g)$$

Formula	Molar Mass
Ni	58.7 $g\cdot mol^{-1}$
$Ni(CO)_4$	171 $g\cdot mol^{-1}$

(A) 24.1% **(B)** 25.0% **(C)** 96.3% **(D)** 100%

Knowledge Required: (1) The relationship between the volume of a gas at standard conditions and the number of moles present. (2) The interpretation of a balanced chemical equation. (3) The criteria for distinguishing essential information from nonessential information.

Thinking it Through: It is not a common practice on ACS exams, but do not assume that all information provided in a question is actually essential to its solution. Rather, decide on a route to the solution that will be the most expedient. Given that 6.25 L of $Ni(CO)_4(g)$ form at standard temperature and pressure conditions, the molar volume of 22.4 L can be used as a conversion factor to find the number of moles of $Ni(CO)_4$ present. Then the coefficients in the balanced chemical equation can be applied, observing that one mole of $Ni(CO)_4$ reacts to produce one mole of Ni. The atomic molar mass for nickel can then be used to find the number of grams of Ni present.

$$6.25\text{ L } Ni(CO)_4 \times \frac{1\text{ mol } Ni(CO)_4}{22.4\text{ L } Ni(CO)_4\text{ at STP}} \times \frac{1\text{ mol Ni}}{1\text{ mol } Ni(CO)_4} \times \frac{58.7\text{ g Ni}}{1\text{ mol Ni}} = 16.4\text{ g Ni}$$

The final step is to find the percent by mass of nickel in the original sample.

$$\%\text{ Nickel} = \frac{16.4\text{ g pure Ni}}{17.0\text{ g impure Ni metal sample}} \times 100 = 96.3\%\text{ Ni}$$

Note you do not need to use the molar mass of $Ni(CO)_4$. Because it is a gas at standard temperature and pressure conditions, the molar volume is a useful conversion factor to change volume to moles.

ST-8. The combustion reaction of C_3H_8O with O_2 is represented by this balanced chemical equation.

$$2C_3H_8O + 9O_2 \rightarrow 6CO_2 + 8H_2O$$

Formula	**Molar Mass**
C_3H_8O	60.1 $g{\cdot}mol^{-1}$
O_2	32.0 $g{\cdot}mol^{-1}$

When 3.00 g C_3H_8O and 7.38 g O_2 are combined, how many moles of which reagent remain?

(A) 0.006 mol O_2

(B) 0.024 mol C_3H_8O

(C) 0.24 mol O_2

(D) 0.18 mol C_3H_8O

Knowledge Required: (1) The identification of the limiting reagent. (2) The method for carrying out mass to mole conversions. (3) The interpretation of a balanced chemical equation.

Thinking it Through: Stoichiometry problems often give an exact mass of one reactant and then either explicitly state or implicitly assume that the other reactant is present in excess. The reactants given in this problem are *not* assumed to be present in stoichiometric amounts; this identifies the question as one involving a limiting reagent. The balanced chemical equation shows that O_2 with C_3H_8O will react in a 9:2 mole ratio. The first task becomes identification of which material will be completely used up, and therefore which one is present in excess. Although there are several approaches to finding the limiting reagent, they all involve the conversion of grams to moles so that the mole ratios can be compared.

$$7.38\text{ g }O_2 \times \frac{1\text{ mol }O_2}{32.0\text{ g }O_2} = 0.231\text{ mol }O_2 \quad \text{and} \quad 3.00\text{ g }C_3H_8O \times \frac{1\text{ mol }C_3H_8O}{60.1\text{ g }C_3H_8O} = 0.0499\text{ mol }C_3H_8O$$

Now these ratios must be compared to the 9:2 mol ratio given in the balanced equation. This can either be done by inspection, or if the ratio is quite different from the stoichiometric ratio, by actual calculation. By inspection, note that there are approximately 0.23 mol of O_2 and 0.05 mol of C_3H_8O. Is this greater or lower than a 9:2 ratio? This is a good time to actually calculate the ratio, for the ratio will be close to 9:2.

$$\frac{0.231\text{ mol }O_2}{0.0499\text{ mol }C_3H_8O} = \frac{4.63\text{ mol }O_2}{1\text{ mol }C_3H_8O} \text{ or } \frac{9.26\text{ mol }O_2}{2\text{ mol }C_3H_8O}$$

Now it is clear that there is more than enough O_2 to react with the C_3H_8O that is present. This identifies C_3H_8O as the limiting reagent, and means that some oxygen will be left over, eliminating choices **(B)** and **(D)** from consideration. There will not be a great deal of O_2 left over, which makes choice **(C)** seem unlikely. To be sure, you can calculate the amount of O_2 that will exactly react with the 0.0499 mol C_3H_8O.

$$0.0499\text{ mol }C_3H_8O \times \frac{9\text{ mol }O_2}{2\text{ mol }C_3H_8O} = 0.225\text{ mol }O_2 \text{ required for a complete reaction with all available } C_3H_8O$$

The difference between the available moles of O_2 (0.231 mol) and the moles of O_2 required for a complete reaction with the available C_3H_8O (0.225 mol) is what will remain after the reaction goes to completion. Subtracting gives 0.006 mol, confirming choice **(A)** as the correct response.

ST-9. What is the maximum mass of $(NH_4)_2SO_4$ that could be formed from 17 kg of NH_3 and 200 kg of solution containing 49% H_2SO_4 by mass? This equation represents the reaction.

$$2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(s)}$$

Formula	**Molar Mass**
NH_3	17 $g{\cdot}mol^{-1}$
H_2SO_4	98 $g{\cdot}mol^{-1}$
$(NH_4)_2SO_4$	132 $g{\cdot}mol^{-1}$

(A) 217 kg

(B) 132 kg

(C) 115 kg

(D) 66 kg

Knowledge Required: (1) The identification of the limiting reagent. (2) The method for carrying out mass–to–mole conversions. (3) The interpretation of a balanced chemical equation.

Thinking it Through: There are two reactants given, so the first step is to determine if there is a limiting reagent. There is no need to change kilograms to grams. The molar mass can be interpreted either as the number of grams per mole or the number of kilograms per kilomole. Compare the number of kilomoles of each reactant, either by inspection or by calculation.

$$17\text{ kg NH}_3 \times \frac{1\text{ kmol NH}_3}{17\text{ kg NH}_3} = 1.0\text{ kmol NH}_3\text{ and}$$

$$200\text{ kg H}_2\text{SO}_4\text{ solution} \times \frac{49\text{ kg H}_2\text{SO}_4}{100\text{ kg H}_2\text{SO}_4\text{ solution}} \times \frac{1\text{ kmol H}_2\text{SO}_4}{98\text{ kg H}_2\text{SO}_4} = 1.0\text{ kmol H}_2\text{SO}_4$$

The chemical equation shows that there is a 2:1 mol ratio, NH_3 to H_2SO_4. Therefore for 1.0 kmol of NH_3, only 0.5 kmol of H_2SO_4 is required, making it the reactant present in excess. NH_3 is the limiting reagent.

$$1.0\text{ kmol NH}_3 \times \frac{1\text{ kmol (NH}_4)_2\text{SO}_4}{2\text{ kmol NH}_3} \times \frac{132\text{ kg (NH}_4)_2\text{SO}_4}{1\text{ kmol (NH}_4)_2\text{SO}_4} = 66\text{ kg (NH}_4)_2\text{SO}_4$$

This is choice **(D).** If you incorrectly choose the sulfuric acid as the limiting reagent, you will obtain 132 kg, which is choice **(B)**. Choice **(A)** is just the direct sum of the two given masses; not a correct approach. Choice **(C)** might be obtained by adding the mass of both NH_3 and pure H_2SO_4, an incorrect use of the Law of Conservation of Mass.

ST-10. What is the percent yield of PbI_2 if 5.00 g of PbI_2 results from a solution containing 10.0 g of $Pb(C_2H_3O_2)_2$ with a solution containing an excess of KI? This is the equation representing the reaction. $Pb(C_2H_3O_2)_{2}(aq) + 2KI(aq) \rightarrow PbI_{2}(s) + 2KC_2H_3O_{2}(aq)$

Formula	**Molar Mass**
PbI_2	461.0 g·mol^{-1}
$Pb(C_2H_3O_2)_2$	325.3 g·mol^{-1}

(A) 17.6% **(B)** 35.3% **(C)** 50.0% **(D)** 70.5%

Knowledge Required: (1) The meaning of percent yield. (2) The method for carrying out mass–to–mole conversions. (3) The interpretation of a balanced chemical equation.

Thinking it Through: The percent yield of a chemical reaction is a ratio of the experimental yield to the maximum amount that could theoretically be produced. This is the relationship.

$$\text{Percent Yield} = \frac{\text{Experimental Yield}}{\text{Theoretical Yield}} \times 100$$

In this problem, the experimental yield of 5.00 g PbI_2 is given. Before finding the percent yield, it is necessary to determine the theoretical yield, which is the maximum amount of product that could be produced. The theoretical yield is based on the given amounts of reactants, taking into consideration the mole ratios of reactants to products revealed in the balanced chemical equation. There is an excess of KI solution. The 10.0 g of $Pb(C_2H_3O_2)_2$ is the limiting reagent and determines the maximum amount of $PbI_2(s)$ that could be produced. Observe that there is a one-to-one mole ratio between the reactant $Pb(C_2H_3O_2)_2$ and the product $PbI_2(s)$.

$$10.0\text{ g Pb(C}_2\text{H}_3\text{O}_2)_2 \times \frac{1\text{ mol Pb(C}_2\text{H}_3\text{O}_2)_2}{325.3\text{ g Pb(C}_2\text{H}_3\text{O}_2)_2} \times \frac{1\text{ mol PbI}_2}{1\text{ mol Pb(C}_2\text{H}_3\text{O}_2)_2} \times \frac{461.0\text{ g PbI}_2}{1\text{ mol PbI}_2} = 14.2\text{ g PbI}_2$$

Now there is enough information to compare the experimental yield of 5.00 g to the theoretical yield of 14.2 g.

$$\text{Percent Yield} = \frac{\text{Experimental Yield}}{\text{Theoretical Yield}} \times 100 = \frac{5.00\text{ g PbI}_2}{14.2\text{ g PbI}_2} \times 100 = 35.3\text{ percent yield}$$

Note: In this case, the balanced equation is given. In other cases, you may have to provide the equation or balance a given skeleton equation before solving the problem.

Practice Questions

1. A compound is found to consist of 34.9% sodium, 16.4% boron and 48.6% oxygen. What is its simplest formula?

(A) $NaBO_2$ (B) $NaBO_3$ (C) $Na_2B_4O_7$ (D) Na_3BO_3

2. Upon analysis, a compound is found to contain 22.8% sodium, 21.8% boron, and 55.4% oxygen. What is its simplest formula?

(A) NaBO (B) NaB_2O_5 (C) $Na_2B_4O_7$ (D) Na_3BO_4

3. A 4.08 g sample of a compound of nitrogen and oxygen contains 3.02 g of oxygen. What is the empirical formula?

(A) NO (B) NO_2 (C) N_2O (D) N_2O_5

4. What is the percent by mass of oxygen in $Ca(NO_3)_2$?

(A) 29.3 % (B) 47.1 % (C) 58.5 % (D) 94.1 %

5. Which of these compounds contains the greatest percentage of nitrogen?

Formula	Molar Mass
$C_6H_3N_3O_7$	229. g·mol^{-1}
CH_4N_2O	60.1 g·mol^{-1}
$LiNH_2$	23.0 g·mol^{-1}
$Pb(N_3)_2$	291. g·mol^{-1}

(A) $C_6H_3N_3O_7$ (B) CH_4N_2O (C) $LiNH_2$ (D) $Pb(N_3)_2$

6. What mass of carbon is present in 0.500 mol of sucrose ($C_{12}H_{22}O_{11}$)?

Formula	Molar Mass
$C_{12}H_{22}O_{11}$	342 g·mol^{-1}

(A) 60.0 g (B) 72.0 g (C) 90.0 g (D) 120. g

7. How many atoms are in 1.50 g of Al?

(A) 0.0556 (B) 18.0 (C) 3.35×10^{22} (D) 2.44×10^{25}

8. A sample of a compound of xenon and fluorine contains molecules of a single type; XeF_n, where n is a whole number. If 9.03×10^{20} of these XeF_n molecules have a mass of 0.311 g, what is the value of n?

(A) 2 (B) 3 (C) 4 (D) 6

9. What mass of carbon is present in 1.4×10^{20} molecules of sucrose ($C_{12}H_{22}O_{11}$)?

Formula	Molar Mass
$C_{12}H_{22}O_{11}$	342 g·mol^{-1}

(A) 1.7×10^{21} g (B) 2.0×10^{22} g (C) 3.3×10^{-2} g (D) 2.8×10^{-3} g

10. A 2.000 g sample of an unknown metal, M, was completely burned in excess O_2 to yield 0.02224 mol of the metal oxide, M_2O_3. What is the metal?

(A) Y (B) Ca (C) Al (D) Sc

11. A 3.41×10^{-6} g sample of a compound is known to contain 4.67×10^{16} molecules. This compound is

(A) CO_2 **(B)** CH_4 **(C)** NH_3 **(D)** H_2O

12. Avogadro's number equals the number of

(A) atoms in one mole of atoms. **(B)** molecules in one mole of O_2.
(C) marbles in one mole of marbles. **(D)** all of the above.

13. The number of atoms in 9.0 g of aluminum is the same as the number of atoms in

(A) 8.1 g of magnesium. **(B)** 9.0 g of magnesium.
(C) 12.1 g of magnesium. **(D)** 18.0 g of magnesium.

14. A single molecule of a certain compound has a mass of 3.4×10^{-22} g. Which value comes closest to the mass of a mole of this compound?

(A) 50 $g \cdot mol^{-1}$ **(B)** 100 $g \cdot mol^{-11}$ **(C)** 150 $g \cdot mol^{-1}$ **(D)** 200 $g \cdot mol^{-1}$

15. What mass of $KClO_3$ will produce 48.0 g of oxygen gas, O_2, if the decomposition of $KClO_3$ is complete?

Formula	**Molar Mass**
$KClO_3$	122.5 $g \cdot mol^{-1}$

(A) 61.3 g **(B)** 74.5 g **(C)** 122.5 g **(D)** 245.0 g

16. What is the maximum mass of aluminum chloride that could be obtained from 6.00 mol of barium chloride and excess aluminum sulfate? This is the balanced equation for the reaction.

$$Al_2(SO_4)_3 + 3BaCl_2 \rightarrow 3BaSO_4 + 2AlCl_3$$

Formula	**Molar Mass**
$BaCl_2$	208.3 $g \cdot mol^{-1}$
$AlCl_3$	133.3 $g \cdot mol^{-1}$

(A) 1250 g **(B)** 801 g **(C)** 534 g **(D)** 134 g

17. A self-contained breathing apparatus uses potassium superoxide, KO_2, to convert the carbon dioxide and water in exhaled air into oxygen, as shown by this equation.

$$4KO_2(s) + 4CO_2(g) + 2H_2O\,(g) \rightarrow 4KHCO_3(s) + 3O_2(g)$$

How many molecules of oxygen gas will be produced from the 0.0468 g of carbon dioxide that is exhaled in a typical breath?

(A) 4.8×10^{20} **(B)** 6.4×10^{20} **(C)** 8.5×10^{20} **(D)** 1.9×10^{21}

18. A mixture containing 9 mol of F_2 and 4 mol of S is allowed to react. This equation represents the reaction that takes place.

$$3F_2 + S \rightarrow SF_6$$

How many moles of F_2 *remain* after 3 mol of S have reacted?

(A) 4 **(B)** 3 **(C)** 1 **(D)** 0

19. When 1.187 g of a metallic oxide is reduced with excess hydrogen, 1.054 g of the metal is produced. What is the metallic oxide?

(A) Ag_2O **(B)** Cu_2O **(C)** K_2O **(D)** Tl_2O

20. How many moles of iron react with 1.75 mol of oxygen gas? The equation for the reaction is:

$$3O_2(g) + 4Fe(s) \rightarrow 2Fe_2O_3(s)$$

(A) 1.31 mol **(B)** 1.75 mol **(C)** 2.33 mol **(D)** 5.25 mol

21. The limiting reagent in a particular reaction can be recognized because it is the reagent that

(A) has the smallest coefficient in the balanced equation.

(B) has the smallest mass in the reaction mixture.

(C) is present in the smallest molar quantity.

(D) would be used up first.

22. Consider this reaction used for the production of lead.

$$2PbO(s) + PbS(s) \rightarrow 3Pb(s) + SO_2(g)$$

What is the maximum mass of lead that can be obtained by the reaction of 57.33 g PbO and 33.80 g of PbS?

Formula	Molar Mass
Pb	$207.2\ g\cdot mol^{-1}$
PbO	$223.2\ g\cdot mol^{-1}$
PbS	$239.3\ g\cdot mol^{-1}$
SO_2	$64.07\ g\cdot mol^{-1}$

(A) 43.48 g (B) 72.75 g (C) 79.83 g (D) 87.80 g

23. What volume of 0.131 M $BaCl_2$ is required to react completely with 42.0 mL of 0.453 M Na_2SO_4? This is the net ionic equation for the reaction.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

(A) 12.1 mL (B) 72.6 mL (C) 145 mL (D) 290 mL

24. In acidic solution, the dichromate ion, $Cr_2O_7^{2-}(aq)$ will oxidize Fe^{2+} to Fe^{3+} and form Cr^{3+}. This net ionic equation represents the reaction that takes place during the reaction.

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$$

What volume of 0.100 M $Cr_2O_7^{2-}(aq)$ is required to oxidize 60.0 mL of 0.250 M $Fe^{2+}(aq)$?

(A) 25.0 mL (B) 42.0 mL (C) 58.4 mL (D) 175 mL

25. Consider this reaction. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

What mass of $CaCO_3$ will produce 8.0 L of CO_2, measured at standard temperature and pressure conditions?

Formula	Molar Mass
$CaCO_3$	$100.\ g\cdot mol^{-1}$

(A) 4.5 g (B) 12.5 g (C) 36 g (D) 280 g

26. When $FeCl_3$ is ignited in an atmosphere of pure oxygen, this reaction takes place.

$$4FeCl_3(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) + 6Cl_2(g)$$

If 3.00 mol of $FeCl_3$ are ignited in the presence of 2.00 mol of O_2 gas, how much of which reagent is present in excess and therefore remains unreacted?

(A) 0.33 mol $FeCl_3$ remains unreacted (B) 0.67 mol $FeCl_3$ remains unreacted

(C) 0.25 mol O_2 remains unreacted (D) 0.50 mol O_2 remains unreacted

27. Ammonia, NH_3, reacts with the hypochlorite ion, OCl^-, to produce hydrazine, N_2H_4. How many moles of hydrazine are produced from 5.85 mol of ammonia if the reaction has a 78.2% yield?

$$2NH_3 + OCl^- \rightarrow N_2H_4 + Cl^- + H_2O$$

(A) 2.29 mol (B) 2.92 mol (C) 4.57 mol (D) 9.15 mol

28. Ammonia can be prepared by the Haber process, shown in this equation.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

If 2 mol of N_2 and 3 mol of H_2 are combined, the amount of NH_3 that would be formed if all of the limiting reactant were used up is known as the

(A) limited yield. **(B)** percent yield. **(C)** product yield. **(D)** theoretical yield.

29. Antimony reacts with sulfur according to this equation.

$$2Sb(s) + 3S(s) \rightarrow Sb_2S_3(s)$$

Formula	Molar Mass
Sb_2S_3	339.7 g·mol^{-1}

What is the percentage yield for a reaction in which 1.40 g of Sb_2S_3 is obtained from 1.73 g of antimony and a slight excess of sulfur?

(A) 80.9% **(B)** 58.0% **(C)** 40.5% **(D)** 29.0%

30. When 4.50 g of Fe_2O_3 is reduced with excess H_2 in a furnace, 2.60 g of metallic iron is recovered. What is the percent yield? This is the equation representing the reaction.

Formula	Molar Mass
Fe_2O_3	159.7 g·mol^{-1}

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$$

(A) 82.6% **(B)** 70.0% **(C)** 57.8% **(D)** 31.5%

Answers to Study Questions

1. A
2. D
3. A
4. B
5. B
6. B
7. C
8. A
9. D
10. B

Answers to Practice Questions

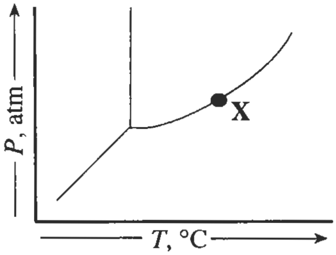
1. A
2. C
3. D
4. C
5. C
6. B
7. C
8. C
9. C
10. D
11. A
12. D
13. A
14. D
15. C
16. C
17. A
18. D
19. B
20. C
21. D
22. C
23. C
24. A
25. C
26. A
27. A
28. D
29. B
30. A

States of Matter / Solutions

The three common states of matter–solids, liquids, and gases–are considered in most general chemistry courses. Both qualitative generalizations and quantitative laws are part of this study. Phase diagrams show the temperature/pressure relationships among the three states. The relative physical properties of the three states are studied, including diffusion and compressibility. For solids, other topics may include bonding, crystal shapes, and solubility rules. For liquids, properties such as miscibility and vapor pressure are included. Properties of gases and mathematical relationships such as the ideal gas laws are either explicitly taught or assumed as a common base of knowledge. Topics considered with solutions are units of concentration, preparation and dilution, and properties associated with the number of solute particles dissolved.

Study Questions

SM-1. According to this phase diagram showing the gas, liquid, and solid phases of a pure substance, what phase or phases can be present at point **X**?



(A) liquid only

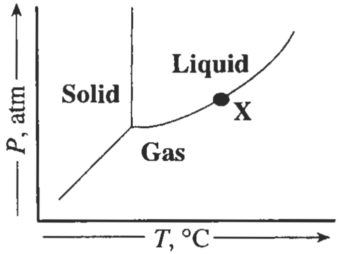
(B) liquid and gas only

(C) solid and gas only

(D) liquid and solid only

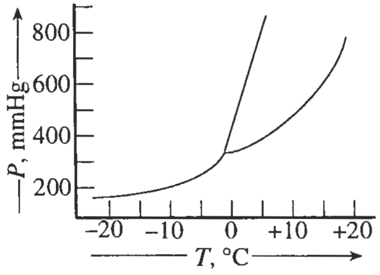
Required Knowledge: (1) The states of matter. (2) The interpretation of phase diagrams.

Thinking it Through: A generalized phase diagram shows how the solid, liquid, and gaseous regions vary with temperature and pressure. The three phases are always in the same relative positions; the slopes of the lines vary considerably. The lines show the boundaries between phases and under those conditions, both phases occur together. Point **X** is located on the phase boundary between liquid and gaseous states, so choice **(B)** is correct.



SM-2. What is the normal melting point of the pure substance **Z**?

Phase Diagram for Substance Z



(A) +18 °C

(B) +4 °C

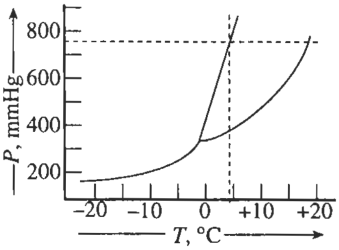
(C) –2 °C

(D) –22 °C

Required Knowledge: (1) States of matter. (2) Interpretation of phase diagrams. (3) Definition of melting point.

Thinking it Through: The normal melting point of a substance is the temperature at which the solid and liquid phases are in equilibrium at standard atmospheric pressure, 760 mmHg. From the graph, the temperature corresponding to 760 mmHg is approximately +4 °C, making choice **(B)**, the correct answer. Choice **(A)** gives the approximate boiling point, not the melting point. Choice **(C)** is the triple point for this substance, the temperature and pressure at which all three states occur in equilibrium. Choice **(D)** has no significance but just appears to be the left end of the curve.

Phase Diagram for Substance Z



SM-3. Which substance meets the requirements: cubic solid; poor electrical conductor in the solid state; good conductor when fused?

(A) sodium chloride
(B) diamond
(C) sulfur
(D) chromium

Knowledge Required: (1) The bonding in solids. (2) The properties associated with bonding types.

Thinking it Through: Solids exhibit a variety of bonding types, each of which can be associated with different properties. This table summarizes the expected relationships.

Type of bonding in solid	**Structure of solid**	**Expected Conductivity of solid**	**Expected Conductivity if solid is fused**
Ionic	crystalline	low	high
Covalent	amorphous or crystalline	low	low
Network covalent	crystalline or amorphous	low	low
Metallic	crystalline	high	high

Of the solids given, ionically bonded sodium chloride is expected to be crystalline, a poor electrical conductor in the solid form, and a good conductor when fused. Diamond, formed of covalently bonded carbon atoms, is a network substance that does not form cubic crystalline patterns, and does not conduct electricity either when solid or fused. None of the allotropic forms of sulfur is expected to conduct electricity. Choice **(D)**, the metal chromium, could possibly form a cubic solid crystalline form, but can be eliminated because it is expected to conduct electricity both when a solid and when fused. The correct choice is **(A),** because sodium chloride is a crystalline solid that is a poor conductor in the solid state and a good conductor when fused.

SM-4. Two pure solid substances, **A** and **B**, each melt at 87.5 °C. An unknown pure solid substance **X** also melts at 87.5 °C. Melting points are obtained for mixtures of **X** with **A**, **X** with **B**, and **A** with **B**. The melting point of each mixture tested is found to be below 87.5 °C. Which conclusion is justified by these data?

(A) **X** is the same as **A** but different from **B**.

(B) **X**, **A**, and **B** are all the same substance.

(C) **X** is different from both **A** and **B**.

(D) **A** and **B** are the same, but **X** is different.

Knowledge Required: (1) The relationship of melting point with purity. (2) The interpretation of experimental data.

Thinking it Through: Pure substances can be differentiated based on the temperature at which the solid and liquid phases are in equilibrium. This temperature is termed the melting point. Each of the pure substances **A**, **B**, and **X** has the *same* melting point. If these were different samples of the same substance, then any mixture of **A**, **B**, and **X** would also have the *same* melting point. This is not consistent with the given observations, so choice **(B)** can be eliminated. So can choice **(D)**, because the question states that substance **A** and **B** are different. If different substances are mixed, even if they have the same melting point when pure, the melting point of the mixture is expected to be *lower* than the melting point of the pure substance. None of the three combinations produces a melting point of 87.5 °C, so all three substances *must* be different. This eliminates choice **(A)** and again eliminates choice **(D)**. This leaves choice **(C)**, in which **X** is different from both substance **A** and substance **B**.

SM-5. The vapor pressure of four different substances at 20 °C is given in the table. Which statement about these substances is correct?

Substance	Vapor pressure, mmHg
1	0.0012
2	18
3	175
4	442

(A) The normal boiling point of **4** should be greater than that of **2**.

(B) The heat of vaporization of **3** should be greater than that of **2**.

(C) The intermolecular forces between molecules of **2** should be greater than those between molecules of **1**.

(D) The surface tension of **2** should be greater than that of **3**.

Knowledge Required: (1) The meaning of term vapor pressure. (2) The correlation of vapor pressure data with other physical properties.

Thinking it Through: Substances with a lower numerical value of vapor pressure have little tendency to change from liquid to gas. Such substances have strong particle-to-particle interactions and/or high average molecular mass. These substances can be expected to have relatively higher heats of vaporization, higher boiling points, and greater surface tension. Larger values of vapor pressure indicate substances with low average molecular mass and/or with very little interaction among the particles. These substances will have relatively lower heats of vaporization, lower boiling points, and less surface tension. Choice **(A)** is not reasonable based on the given trend in vapor pressure, because substance **4** has a higher vapor pressure than substance **2**, indicating it will have a lower boiling point. Choices **(B)** and **(C)** are also reversed from the expected trend. Choice **(D)** is the most reasonable. Substance **2** with its lower vapor pressure than substance **3**, is expected to have a greater surface tension.

SM-6. A mixture of 0.5 mol of CH_4, 0.5 mol of H_2, and 0.5 mol of SO_2 is introduced into a 10.0-L container at 25 °C. If the container has a pinhole leak, which describes the relationship between the partial pressures of the individual components in the container after 3 hours?

(A) $P_{SO_2} > P_{CH_4} > P_{H_2}$

(B) $P_{SO_2} < P_{CH_4} < P_{H_2}$

(C) $P_{SO_2} < P_{CH_4} > P_{H_2}$

(D) $P_{SO_2} = P_{CH_4} = P_{H_2}$

Required Knowledge: (1) The behavior of gases. (2) The kinetic–molecular theory. (3) The qualitative understanding of Graham's Law of Effusion.

Thinking it Through: Equal amounts of each gas are present, so the partial pressure of each gas remaining in the container after 3 hours will depend on the rate with which each escapes. The lightest gases will escape most quickly through a pinhole leak. The molar mass of CH_4 is 18 $g{\cdot}mol^{-1}$, of H_2 is 2 $g{\cdot}mol^{-1}$, and of SO_2 is 64 $g{\cdot}mol^{-1}$. Hydrogen will escape most quickly, followed by methane, and then sulfur dioxide. The partial pressure of the each gas remaining in the container will therefore be in reverse order, $P_{SO_2} > P_{CH_4} > P_{H_2}$. This is choice **(A)**.

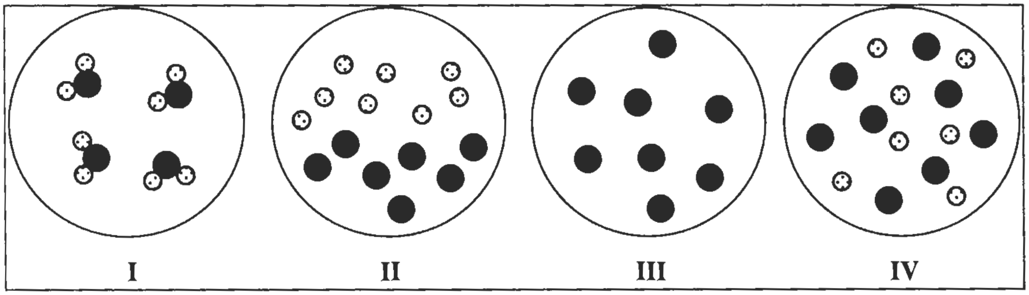
SM-7. Which is true about equal volumes of CH_4 and O_2 gases at 20 °C and 1 atm pressure?

- **(A)** The CH_4 sample has a mass that is one-half that of the O_2 sample.
- **(B)** The number of O_2 molecules is twice as large as the number of CH_4 molecules.
- **(C)** The average kinetic energy of the O_2 molecules is one-half that of the CH_4 molecules.
- **(D)** The average velocity of the O_2 molecules is one-half that of the CH_4 molecules

Knowledge Required: (1) The understanding of Avogadro's Principle. 2) The relationships of average molecular speed and kinetic energy to temperature and pressure conditions.

Thinking it Through: The two gases, CH_4 and O_2, are at the same temperature and pressure conditions. Avogadro's Principle states that equal volumes of any gas under the same temperature and pressure conditions will contain the same number of molecular particles. Although this straightforward answer is not given as one of the choices, it does eliminate choice **(B)**. If the molar masses of the two gases are considered, 16 $g{\cdot}mol^{-1}$ for CH_4 and 32 $g{\cdot}mol^{-1}$ for O_2, the 1:2 ratio is revealed. This means that even though an equal number of particles are present, only half the mass of CH_4 is present, making choice **(A)** the correct answer. Choice **(C)** is incorrect as the average kinetic energy is directly proportional to the temperature, which is the same for both gases. Choice **(D)** is also incorrect for the average velocity is inversely proportional to the square root of the mass of the molecules, an application of Graham's Law.

SM-8. Which microscopic representation best represents a solution?



(A) I (B) II (C) III (D) IV

Required Knowledge: (1) The definition of a solution. (2) The particulate representation of particles forming solutions.

Thinking it Through: Solutions are homogeneous mixtures of two or more substances. They may exist in all three phases, although often in general chemistry solutions are aqueous solutions meaning that the solvent is water. Choice **(A)** cannot represent a solution, as there is only one type of molecular particle represented. Choice **(B)** has two different types of particles, but they appear to be in distinct layers. Choice **(C)** again has only one type of particle. Choice **(D)** is the best representation as it shows two types of particles distributed relatively homogeneously.

SM-9. A solution is made by dissolving 60 g of NaOH ($M = 40\ g{\cdot}mol^{-1}$) in enough distilled water to make 300 mL of a stock solution. What volumes of this solution and distilled water, when mixed, will result in a solution that is approximately 1 M NaOH?

	mL stock solution	**mL distilled water**
(A)	20	80
(B)	20	100
(C)	60	30
(D)	60	90

Knowledge Required: (1) The definition of molarity. (2) The knowledge of vocabulary associated with solutions. (3) The procedures for preparing dilute solutions.

Thinking it Through: Molarity is commonly used to express the concentration of a solution.

$$\mathrm{M} = \frac{\text{moles of solute}}{\text{L of solution}} = \frac{\text{grams of solute}}{\text{molar mass of solute} \times \text{L of solution}}$$

The molarity of the solution first prepared can be calculated by substituting the given values. The volume of solution, 300 mL, should be expressed in liters, 0.300 L.

$$\mathrm{M} = \frac{\left[60\text{ g NaOH} \times \left(\frac{1\text{ mol NaOH}}{40\text{ g}}\right)\right]}{0.300\text{ L}} = \frac{5\text{ mol}}{\text{L}} = 5\text{ M}$$

This solution, called the stock solution, will now be used to prepare a solution that is approximately 1 M NaOH. The number of moles of NaOH in the diluted solution will be the same as it was in the stock solution; it will just be dispersed in a larger volume. Since we are seeking a volume in milliliters, it is more convenient to express the molarity as millimoles per milliliter (which is exactly the same as moles per liter).

$$\text{millimoles NaOH in stock solution} = \text{millimoles of NaOH in diluted solution}$$

Assuming 20 mL of stock solution,

$$(20\text{ mL})_{\text{stock}} \times (5\text{ mmol/mL})_{\text{stock}} = V_{\text{new solution}} \times (1\text{ mmol/mL})_{\text{new solution}}$$

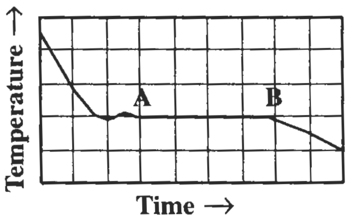
$$V_{\text{new solution}} = \left(\frac{20\text{ mL} \times 5\text{ mmol/mL}}{1\text{ mmol/mL}}\right) = 100\text{ mL}$$

The total volume of the new solution is approximately equal to the volume of stock solution (20 mL) plus the water added (x mL) to produce 100 mL. That comes out to 80 mL of water added, which is intended to be the correct choice.

$$x\text{ mL} = 100\text{ mL} - 20\text{ mL} = 80\text{ mL}$$

You've probably noticed that we use the word *approximately* when describing the concentration and volume of the new solution. In fact, adding 80 mL of water to 20 mL of stock solution produces slightly less than 100 mL of solution. The concentration of NaOH in the diluted solution is slightly greater than 1 M. This is because the densities of NaOH solutions are greater than 1 g/mL. As the NaOH solution is diluted, the density of the solution approaches that of water, which is 1 g/mL. Nonetheless, 80 mL, choice **(A),** is still the best. This is a 1:5 dilution. Choice **(B)** gives a 1:6 dilution, but you may be drawn to it if you neglect to consider that it is not just the water added, but the *total volume* of the solution that must be used. Choice **(C)** results in a 60: 90 or a 2:3 dilution, and choice **(D)** results in a 2:5 dilution. None of these produce a 1 M solution.

SM-10. Given the cooling curve of one gram of a pure liquid, the length of the line **AB** depends on



(A) the specific heat of the pure solid.

(B) the specific heat of the pure liquid.

(C) the heat of melting of the pure substance.

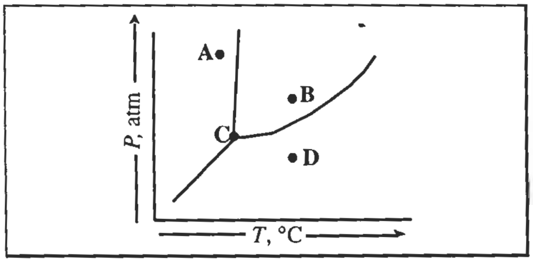
(D) the melting point of the pure substance.

Knowledge Required: (1)The meaning of specific heat, heat of melting, and melting point. (2) The interpretation of experimental data.

Thinking it Through: As a pure liquid cools undisturbed in a clean container, the temperature usually dips briefly below the melting point of the solid. When solid crystals begin to form, the temperature rises to the melting point of the solid (point **A**), where it remains until all the liquid has finally been converted to solid (point **B**). Neither **A** nor **B** are reasonable choices, because both liquid and solid are present from point **A** to point **B**. Choice **(C)** recognizes that the heat being removed from the liquid goes into changing the potential energy of the molecules. Kinetic energy remains the same. Choice **(D)** is an intensive property (temperature) rather than an extensive property (heat). The cooling curve interprets heat being removed from the liquid.

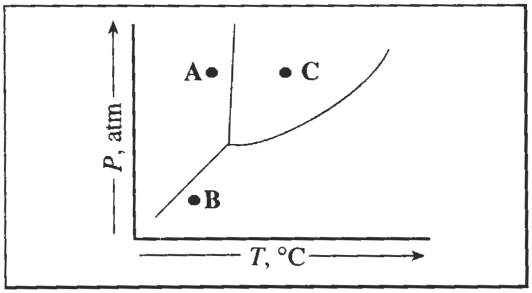
Practice Questions

1. In the phase diagram, which transition represents the condensation of a gas to a liquid?



(A) B to A (B) D to B (C) C to D (D) A to D

2. Consider the phase diagram of a pure compound. Which statement applies?



(A) The path **A** → **C** represents sublimation.

(B) Following the path **A** → **B** → **C,** the compound would first liquefy and then vaporize.

(C) If the compound is in state **A**, continued reduction of the pressure (at constant temperature) will cause it to melt.

(D) None of these statements is correct.

3. A particular solid is soft, a poor conductor of heat and electricity, and has a low melting point. Generally, such a solid is classified as

(A) ionic. (B) molecular.

(C) metallic. (D) network covalent.

4. Carbon dioxide, CO_2, in the form of dry ice would be classified as

(A) an ionic solid. (B) a molecular solid.

(C) a polymeric solid. (D) a metallic solid.

5. The melting point of an impure compound is generally

(A) higher than that of the pure solid.

(B) the same as that of the pure solid.

(C) lower than that of the pure solid.

(D) a function of the vapor pressure of the impurity.

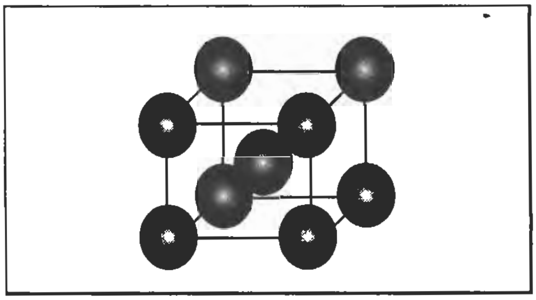
6. What is the vapor pressure of a solution with a benzene to octane molar ratio of 2:1?

Vapor Pressure at 50 °C	
benzene	280 mmHg
octane	400 mmHg

(A) 120 mmHg **(B)** 320 mmHg **(C)** 400 mmHg **(D)** 680 mmHg

7. Lithium crystallizes in a body-centered cubic unit cell. What is the mass of one unit cell? Report your answer in grams.

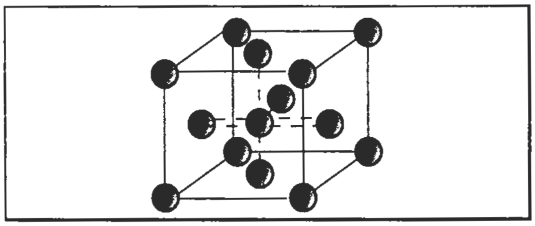
● = lithium atom



(A) 1.15×10^{-23} g **(B)** 2.30×10^{-23} g **(C)** 5.75×10^{-23} g **(D)** 1.04×10^{-22} g

8. Copper crystallizes in a face-centered cubic lattice. If the edge of the unit cell is 362 pm, what is the radius of the copper atom?

● = copper atom



(A) 128 pm **(B)** 171 pm **(C)** 181 pm **(D)** 255 pm

9. Which factor affects the vapor pressure of a liquid?

(A) temperature **(B)** atmospheric pressure

(C) volume of the liquid **(D)** surface area of the liquid

10. A gas or vapor may be liquefied only at temperatures

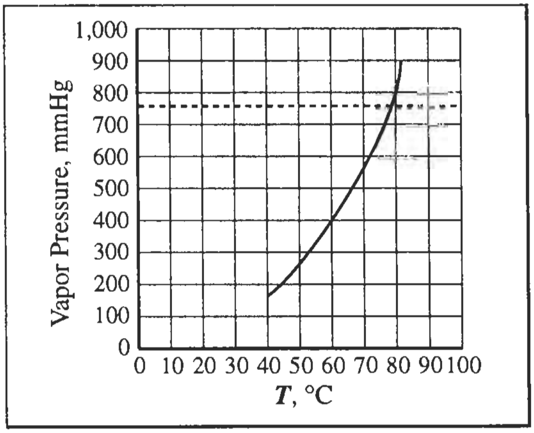
(A) equal to the normal boiling point.

(B) above the normal boiling point.

(C) above the critical temperature.

(D) at or below the critical temperature.

11. The graph shows how the vapor pressure of a liquid changes with temperature. Select the choice that best indicates the degree of correctness of this statement: *"The normal boiling point of the liquid is 78 °C."*



(A) The statement is true.

(B) The statement is probably true; additional data would be needed for a final decision.

(C) The statement is probably false; additional data would be needed for a final decision.

(D) The statement is false.

12. What is the molar mass of an ideal gas if a 0.622 g sample of this gas occupies a volume of 300. mL at 35 °C and 789 mm Hg?

(A) 44.8 $g \cdot mol^{-1}$ **(B)** 48.9 $g \cdot mol^{-1}$ **(C)** 50.5 $g \cdot mol^{-1}$ **(D)** 54.5 $g \cdot mol^{-1}$

13. Which set of temperature and pressure conditions will cause a gas to exhibit the greatest deviation from ideal gas behavior?

(A) 100 °C and 4 atm **(B)** 100 °C and 2 atm

(C) –100 °C and 4 atm **(D)** 0 °C and 2 atm

14. A 500 mL gas sample is collected over water at a pressure of 740 mmHg and 25 °C. What is the volume of the dry gas at STP? (STP = 1 atm and 0 °C.)

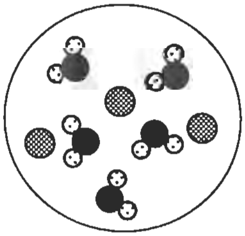
Vapor Pressure of H_2O at 25 °C
24 mmHg

(A) $500 \times \frac{740+24}{760} \times \frac{298}{273}$ **(B)** $500 \times \frac{740-24}{760} \times \frac{273}{298}$

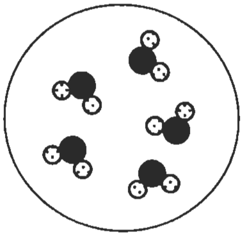
(C) $500 \times \frac{760}{740-24} \times \frac{273}{298}$ **(D)** $500 \times \frac{760}{740+24} \times \frac{298}{273}$

15. Which diagram represents the most concentrated solution?

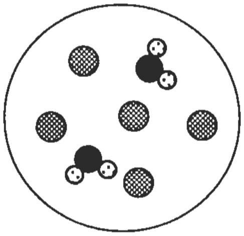
Note: represents a solute particle and represents a water molecule.



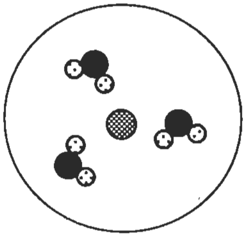
I



II



III



IV

(A) I **(B)** II **(C)** III **(D)** IV

16. What is the molarity of a solution made by dissolving 8.56 g of sodium acetate in water and diluting to 750.0 mL?

Formula	Molar Mass
$NaC_2H_3O_2$	82.03 g·mol^{-1}

(A) 5.30 M (B) 0.139 M (C) 0.104 M (D) 0.0783 M

17. A student wants to prepare 250. mL of 0.10 M NaCl solution. Which procedure is most appropriate?

Formula	Molar Mass
NaCl	58.4 g·mol^{-1}

(A) Add 5.84 g of NaCl to 250. mL of H_2O.

(B) Add 1.46 g of NaCl to 250. mL of H_2O.

(C) Dissolve 5.84 g of NaCl in 50 mL of H_2O and dilute to 250. mL.

(D) Dissolve 1.46 g of NaCl in 50 mL of H_2O and dilute to 250. mL

18. What volume of 12 M HCl solution is required to prepare exactly 500. mL of a 0.60 M HCl solution?

(A) 10. mL (B) 14 mL (C) 25 mL (D) 40. mL

19. In which set are the substances arranged in order of decreasing solubility in water?

(A) $Al(OH)_3 > Mg(OH)_2 > NaOH$ (B) $BaSO_4 > CaSO_4 > MgSO_4$

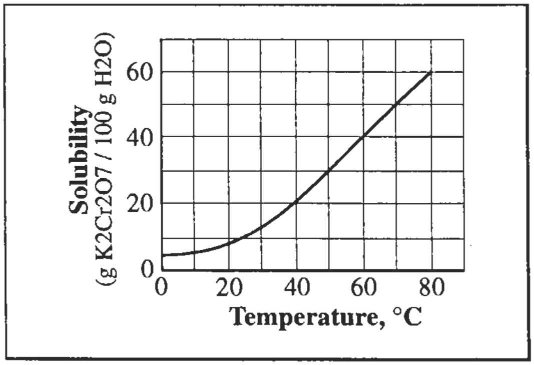
(C) $CaCO_3 > NaHCO_3 > Na_2CO_3$ (D) $AgCl > AgBr > AgI$

20. The solubility of a substance is 60 g per 100 mL of water at 15 °C. A solution of this substance is prepared by dissolving 75 g in 100 mL of water at 75 °C. The solution is then cooled slowly to 15 °C without any solid separating. The solution is

(A) supersaturated at 75 °C. (B) supersaturated at 15 °C.

(C) unsaturated at 15 °C. (D) saturated at 15 °C.

21. A mixture of 100 g of $K_2Cr_2O_7$ and 200 g of water is stirred at 60 °C until no more of the salt dissolves. The resulting solution is poured off, leaving the undissolved solid behind. The solution is now cooled to 20 °C. What mass of $K_2Cr_2O_7$ crystallizes from the solution during the cooling?



(A) 24 g (B) 31 g (C) 43 g (D) 62 g

22. What mass of water is needed to dissolve 292.5 g of NaCl to produce a 0.25 *m* aqueous solution?

Formula	Molar Mass
NaCl	58.5 g·mol^{-1}

(A) 20 kg (B) 5.0 kg (C) 0.80 kg (D) 0.050 kg

23. What is the mole fraction of water in 200. g of 95% (by mass) ethanol, C_2H_5OH?

Formula	Molar Mass
C_2H_5OH	46 g·mol^{-1}

(A) 0.050 (B) 0.12 (C) 0.56 (D) 0.88

24. 800 g of ethanol, C_2H_5OH, was added to 8.0×10^3 g of water. How much would this lower the freezing point?

Freezing Point Depression Constant
K_f for water = 1.86 °C·m^{-1}

(A) 3.2 °C **(B)** 4.1 °C **(C)** 8.2 °C **(D)** 16 °C

25. The edge of a body-centered-cubic unit cell (which contains two atoms per unit cell) of an element **Y** was found to be 3.16×10^{-8} cm. The density of the metal is 19.35 $g \cdot cm^{-3}$. What is the approximate molar mass of **Y**?

(A) 65.4 $g \cdot mol^{-1}$ **(B)** 92.0 $g \cdot mol^{-1}$ **(C)** 184 $g \cdot mol^{-1}$ **(D)** 238 $g \cdot mol^{-1}$

26. What is the number of nearest neighbors in a body-centered-cubic lattice?

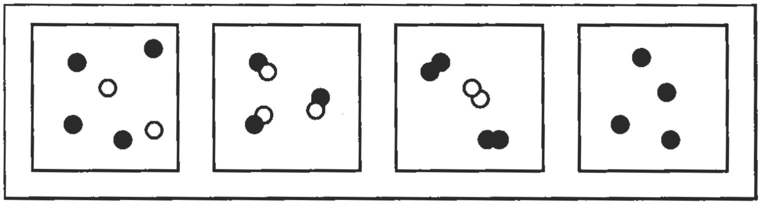
(A) 12 **(B)** 8 **(C)** 6 **(D)** 4

27. Carbon dioxide, CO_2, in the form of dry ice would be classified as

(A) an ionic solid. **(B)** a polymeric solid.

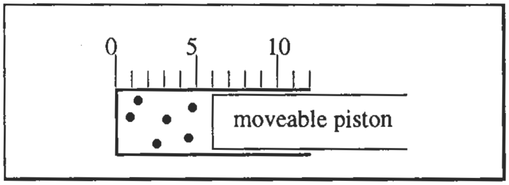
(C) a molecular solid. **(D)** a network solid.

28. Which diagrams represent pure substances?

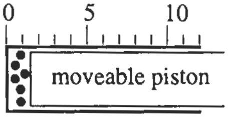


(A) **1 and 2** **(B)** **1 and 3** **(C)** **2 and 3** **(D)** **2 and 4**

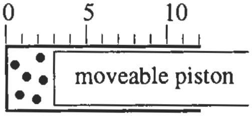
29. Which diagram best represents the final system, if the pressure of the gas in this cylinder were doubled and the temperature increased from 200 K to 400 K?



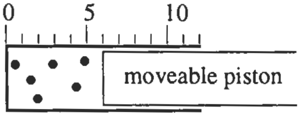
(A)



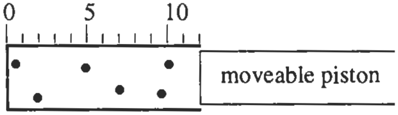
(B)



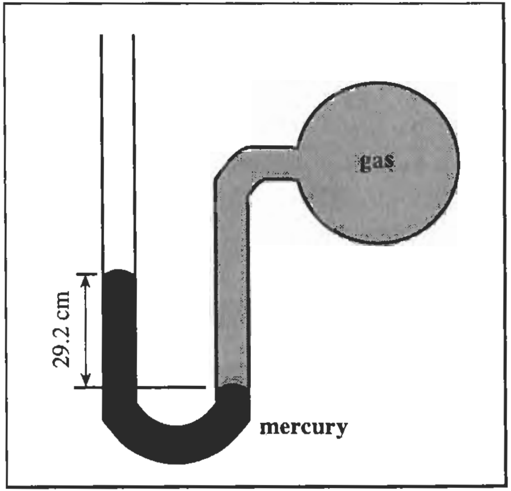
(C)



(D)



30. An open-ended mercury manometer is used to measure the pressure exerted by a trapped gas as shown in the figure. Atmospheric pressure is 749 mmHg. What is the pressure of the trapped gas?



(A) 292 mmHg

(B) 457 mmHg

(C) 749 mmHg

(D) 1041 mmHg

Answers to Study Questions

1. B
2. B
3. A
4. C
5. D
6. A
7. A
8. D
9. A
10. C

Answers to Practice Questions

1. B
2. D
3. B
4. B
5. C
6. B
7. B
8. A
9. A
10. D
11. A
12. C
13. C
14. B
15. C
16. B
17. D
18. C
19. D
20. B
21. D
22. A
23. B
24. B
25. C
26. B
27. C
28. D
29. C
30. D

Energetics

Energetics is a broad area that considers the nature of energy and its relationship with chemical and physical changes. Basic definitions of the vocabulary and units to express energy changes are important aspects of study, and must be mastered before building conceptual understanding. Heat flow under different conditions of pressure and temperature, calorimetry, use of tabulated enthalpy data for standard heats of formation, bond energies, and Hess's Law are typical topics that surround the First Law of Thermodynamics. An examination of spontaneous processes and a molecular interpretation of entropy lead to an understanding of the Second Law of Thermodynamics. Gibbs Free Energy and its relationship to equilibrium are the last areas included in the study of energetics.

EN-1. A 10.0 g sample of silver is heated to 100.0 °C and then added to 20.0 g of water at 23.0 °C in an insulated calorimeter. At thermal equilibrium, the temperature of the system was measured as 25.0 °C. What is the specific heat of silver?

Specific Heat Data	
$H_2O(l)$	$4.184\ J{\cdot}g^{-1}{\cdot}°C^{-1}$

(A) $0.053\ J{\cdot}g^{-1}{\cdot}°C^{-1}$ **(B)** $0.22\ J{\cdot}g^{-1}{\cdot}°C^{-1}$ **(C)** $4.5\ J{\cdot}g^{-1}{\cdot}°C^{-1}$ **(D)** $8.4\ J{\cdot}g^{-1}{\cdot}°C^{-1}$

Knowledge Required: (1) The principles of heat flow. (2) The meaning of the term specific heat. (3) The methods for carrying out calorimetry calculations.

Thinking it Through: When the warmer silver is added to the cooler water in an insulated calorimeter, heat flow will take place from the silver to the water until thermal equilibrium is reached. Energy is conserved in this process and the heat lost by the silver is gained by the water, an illustration of the First Law of Thermodynamics. This law is also known as the Law of Conservation of Energy. The quantity of heat exchanged in this experiment is dependent on three factors—the amount of material, the heat exchanging capacity of the material as expressed by the specific heat, and the temperature change the material undergoes. This is the general relationship.

$$\text{heat} = \text{mass} \times \text{specific heat} \times \text{change in temperature: } J = g \times \frac{J}{g \cdot °C} \times (T_2 - T_1)\ °C$$

Given that the heat lost by the silver must be gained by the water, and assuming no heat loss, the relationship can be expressed in this manner. The symbol *s* represents the specific heat.

$$\text{heat lost} + \text{heat gained} = 0$$

$$10.0\,g \times s \times (100.0\ °C - 25.0\ °C) + 20.0\,g \times \frac{4.184\,J}{g \cdot °C} \times (23.0\ °C - 25.0\ °C) = 0$$

$$s = \frac{20.0\,g \times \dfrac{4.184\,J}{g \cdot °C} \times 2.0\ °C}{10.0\,g \times 75.0\ °C}$$

$$s = \frac{0.22\ J}{g \cdot °C}$$

This is choice **(B)**. Note that this is a reasonable value for silver compared with water's large specific heat. You know from experience that a silver spoon in a cup of hot coffee will quickly become too warm to touch. Water, with its large value for specific heat, warms and cools more slowly. If you solve the equation incorrectly in the last step and divide 750 by 167 rather than the correct 167 by 750, you will end up with choice **(C)**. If you have chosen choice **(A)**, you have neglected to use the specific heat of water. Choice **(D)** results from using an incorrect temperature change of 77 °C for both the silver and the water, neglecting the equilibrium temperature change.

EN-2. During the part of the cycle when heat is removed from the food compartment of an electric refrigerator, the refrigerant undergoes a change from a

(A) liquid to a gas. **(B)** gas to a liquid.

(C) liquid to a solid. **(D)** solid to a liquid.

Knowledge Required: (1) The principles of heat flow. (2) The energy changes during phase changes.

Thinking it Through: If heat is *removed from* the food compartment, it must be *absorbed by* the refrigerant, so you will need to identify those changes in state that are *endothermic*. Both choices **(A)** and **(D)** describe changes in state that will absorb heat; choices **(B)** and **(C)** both involve condensation reactions that release heat so they can be eliminated from consideration. Choosing between **(A)** and **(D)** depends on the fact that it is far easier to circulate and compress fluids than it is to engineer an electric refrigerator based on the phase change from solid to liquid. This is, however, the phase change used in an old-fashioned icebox or your picnic cooler if you load it up with ice blocks or cubes. You may also know that generally the heat of vaporization for a substance is considerably higher than its heat of liquefaction, making the phase change from liquid to gas energetically favored.

EN-3. What is the net energy released in this reaction?

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

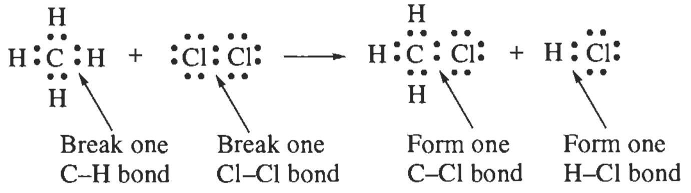
Bond Energies, kJ·mol^{-1}

H–H	431	C–Cl	327
Cl–Cl	239	C–H	410
H–Cl	427	C–C	335

(A) 105 kJ **(B)** 188 kJ **(C)** 754 kJ **(D)** 1403 kJ

Knowledge Required: (1) The meaning of bond energy. (2) The energy changes that take place when bonds are broken and formed.

Thinking it Through: Bond energy, also called by the more descriptive name of bond-dissociation energy, is the energy required to break a bond when the substance is in the gas phase. It *always requires* energy to break bonds, so values for bond energies are always tabulated with a positive sign implied. However, when a given bond forms in the gas phase, it will *always release* that same amount of bond energy. It is the interplay between the bonds broken and the bonds formed that will determine if the reaction overall is endothermic or, as is the case here, exothermic.



There are two bonds to be broken. For the C–H bond, 410 kJ of energy are required per mole. For the Cl–Cl bond, 239 kJ are required per mole. The total energy that must be used is 649 kJ.

There are two bonds that are formed. For the C–Cl bond, 327 kJ of energy are released. For the H–Cl bond, 427 kJ are released. The total energy released is 754 kJ.

Overall, more energy is released in forming bonds than was absorbed in breaking bonds. This defines an exothermic reaction and there is a net energy release of (754kJ – 649 kJ), which equals 105 kJ. This is choice **(A).** Choosing **(C)** means that only the energy released was considered, not the *net* energy released. Choice **(B)** has only focused on the energy required for breaking the Cl–Cl bond relative to that released in forming the H–Cl bond. The other bond energy changes have been ignored. Choice **(D)** is the inappropriate combination of both the energy required and the energy released.

Notes: Bond energies are average experimental values and there is some variation in their values in different questions. Asking for the enthalpy change or ΔH_{rxn} is equivalent to asking for the energy change for this gas phase reaction. Remember, however, that values of ΔH_{rxn} must follow sign conventions. A positive sign is associated with an endothermic reaction and a negative sign with an exothermic reaction.

EN-4. What mass of benzene, $C_6H_6(l)$, must be burned in a bomb calorimeter to raise its temperature by 15 °C?

Thermodynamic Data

$\Delta H^0_{combustion}(C_6H_6(l))$	–41.9 kJ·g^{-1}
Calorimeter Constant	1.259 kJ·°C^{-1}

(A) 0.45 g **(B)** 2.8 g **(C)** 3.5 g **(D)** 35 g

Knowledge Required: (1) The principles of bomb calorimetry. (2) The meaning of heats of combustion.

Thinking it Through: A bomb calorimeter is an insulated container that contains a reaction chamber designed to withstand high pressures. The reaction chamber, or bomb, is surrounded by water that absorbs the heat of the reaction. This experimental device is often used to study reactions at constant volume, particularly the combustion reactions of organic compounds. A sample of the compound being burned is placed in the reaction chamber that is then sealed and pressurized with oxygen. An electric current is passed through a thin wire that gets hot enough to initiate the combustion reaction. Heat is given off during the reaction and that heat is absorbed by the surroundings, causing the measured temperature of the water to rise. In this case, the heat capacity of the calorimeter is given, having been previously determined experimentally. This is called the calorimeter constant. It means that it takes 1.259 kJ of energy to raise the temperature of the reaction chamber's surroundings by one degree Celsius. The value of the heat of combustion is also given, showing that benzene will give off 4.19 kJ of heat energy for every gram of benzene burned. The heat lost by the benzene burning is equal to the heat gained by the surroundings, assuming no heat loss. Let x be the number of grams of benzene.

$$\text{heat evolved} + \text{heat gained} = 0$$

$$x \times \frac{41.9\,\text{kJ}}{\text{g}} + 15\,^\circ\text{C} \times \frac{1.259\,\text{kJ}}{^\circ\text{C}} = 0$$

$$x = 0.45\ \text{g}$$

This is choice **(A)**. If you neglected to use the calorimeter constant, you might choose choice **(B)** in error. If you solved this equation incorrectly, you might choose choice **(C)**. Choice **(D)** could be chosen incorrectly if the 15° temperature change was ignored.

Notes: Often problems of this type will involve the heat of combustion in units of kJ per mole rather than per gram. The molar mass of the substance undergoing combustion can be used to make the necessary conversions.

EN-5. Use the heats of formation, ΔH_f^0, in the table to determine ΔH for this reaction.

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$$

Compound	ΔH_f^0, kJ•mol^{-1}
$C_2H_2(g)$	+227
$H_2O(g)$	–242
$CO_2(g)$	–393

(A) –1602 kJ **(B)** –1829 kJ **(C)** –2283 kJ **(D)** –2510 kJ

Knowledge Required: (1) The meaning of standard heats of formation. (2) The methods of using heats of formation to calculate heats of reaction.

Thinking it Through: The enthalpy change for any reaction occurring at constant pressure can be calculated from the given or tabulated values of standard heats of formation for both reactants and products. It is necessary to sum the heats of formation for all reaction products, being sure to multiply each molar heat of formation by the coefficient of that substance given in the balanced chemical equation. From this total, it is necessary to subtract the sum of the heats of formation for all of the reactants, again multiplying by the coefficients in the balanced chemical equation. This is the generalization for the process.

$$\Delta H^0_{\text{rxn}} = \sum n\,\Delta H_f^0(\text{products}) - \sum m\,\Delta H_f^0(\text{reactants})$$

The symbol $\sum$ (sigma), means "the sum of" and n and m are the total of the coefficients of the products and reactants, respectively. To apply this generalization in this question, use the given values from the table and recall that the standard enthalpy of formation for any element in its standard state is zero. Oxygen gas is an element in its standard state, so no value is given in the table.

$$\Delta H^0_{\text{rxn}} = [(4\,\Delta H_f^0(CO_2) + 2\,\Delta H_f^0(H_2O)] - [2\,\Delta H_f^0(C_2H_2) + 5\,\Delta H_f^0(O_2)]$$

$$\Delta H^0_{\text{rxn}} = [(4 \times (-393\ \text{kJ}) + 2 \times (-242\ \text{kJ})] - [2 \times (+227\ \text{kJ}) + 5 \times (0\ \text{kJ})]$$

$$\Delta H^0_{\text{rxn}} = -2510\ \text{kJ}$$

This is choice **(D)**. Common errors in this type of question are forgetting to use the coefficients or reversing the signs and subtracting the products from the reactants. Various coefficient and sign errors lead to the incorrect answers in choices **(A)** through **(C)**.

EN-6 Given:

Equation 1: $SO_2(g) \rightarrow S(s) + O_2(g)$ $\Delta H = +300$ kJ

Equation 2: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -200$ kJ

Use this information to calculate the heat of formation of $SO_3(g)$.

(A) –500 kJ·mol^{-1} **(B)** –400 kJ·mol^{-1} **(C)** +100 kJ·mol^{-1} **(D)** +200 kJ·mol^{-1}

Knowledge Required: (1) The definition of enthalpy change, ΔH. (2) The definition of heat of formation, ΔH_f^0 (3) The meaning of Hess's Law.

Thinking it Through: The change in enthalpy for a chemical reaction is equal to the heat that is absorbed or released in a chemical reaction taking place at constant temperature and pressure. Enthalpy is an example of a *state function*, one that depends only on the initial and final states of the reactants and products. Enthalpy changes also depend on the amount of material present. Equations for two chemical reactions and their accompanying enthalpy changes are given in this question. However, what is asked for is the *heat of formation*, ΔH_f^0, for $SO_3(g)$.

$$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H_f^0 = ?\ \text{kJ·mol}^{-1}$$

This will be the enthalpy change associated with the formation of SO_3 from its elements, all in their standard states at 25 °C and one atmosphere of pressure. Often it is difficult to carry out such a seemingly straightforward reaction and measure its heat. It is often more convenient to algebraically combine equations and their enthalpies. Chemical equations and the enthalpy changes that accompany them can be combined algebraically only because ΔH does not depend on the path from a set of reactants to a set of products. Rather, it only depends on the change from initial to final states. *Hess's Law* states that if a reaction is carried out in a series of steps, ΔH for the overall reaction can be calculated from the sum of the enthalpy changes for the individual steps. Given experimental data can be changed in any way that is algebraically convenient, so long as the accompanying enthalpy change is also adjusted. For example, if an equation is reversed, the sign of the enthalpy change must be reversed. If an equation is multiplied by a factor, the enthalpy must be multiplied by that same factor. Applying this in this question, and keeping an eye on the desired equation, the first reaction will need to be reversed so the sign of the enthalpy change is also reversed. The second reaction and its enthalpy change is multiplied by 1/2.

Equation 1: $SO_2(g) \rightarrow S(s) + O_2(g)$ $\Delta H = +300$ kJ becomes $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -300$ kJ

Equation 2: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -200$ kJ becomes $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$ $\Delta H = -100$ kJ

Adding the transformed equations together gives:

$$S(s) + O_2(g) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_2(g) + SO_3(g) \qquad \Delta H = (-300\ \text{kJ}) + (-100\ \text{kJ}) = -400\ \text{kJ}$$

Combining like terms and canceling substances that appear on both sides of the equation gives the target equation.

$$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H_f = -400\ \text{kJ·mol}^{-1}$$

This is choice **(B)**. You might pick choice **(A)** in error if you forget to reverse the sign of the enthalpy for Equation 1. If you forgot the sign reversal but also neglected to cut the enthalpy associated with the second equation in half, then you might have chosen choice **(C)**. Choice **(D)** might be selected if the second equation were correctly cut in half, but also reversed and added to **Equation 1**.

EN-7. Which change is likely to be accompanied by an increase in entropy?

(A) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at 25 °C

(B) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ at 25 °C

(C) $CO_2(s) \rightarrow CO_2(g)$ at –70 °C

(D) $H_2O(g) \rightarrow H_2O(l)$ at 100 °C

Knowledge Required: (1) The meaning of the term *entropy*. (2) The interpretation of chemical equations.

Thinking it Through: Entropy is a thermodynamic quantity that expresses the disorder or randomness in a system. Considering whether the reactants or the products are more randomly arranged can identify the change accompanied by the greatest increase in entropy. In choice **(A)**, all of the particles are present in gas phase and there is a change from four moles of gas of diatomic gases to only two moles of more complex ammonia molecules. This system is becoming more ordered, a process likely to produce a decrease in entropy. Choice **(B)** is forming a highly ordered crystal from ions in solution, so once more the process is predicted to be accompanied by a decrease in entropy. Choice **(C)**, the correct choice, will have an increase in entropy, for solid carbon dioxide is changing to gaseous carbon dioxide, a highly disorganized state. CO_2 molecules in the gas phase have many more opportunities to vibrate and will have much higher entropy than the condensed solid phase. Choice **(D)** represents a condensation from the gas to the liquid states; this again will be a decrease, not an increase in randomness. Do not be misled by the temperatures that are given. Although the term $T\Delta S$ gives the total energy contribution in a chemical change from the temperature multiplied by the change in entropy, it is only the change in entropy that is asked in this question.

EN-8. Under which circumstance would the free energy change for a reaction be relatively temperature independent?

(A) ΔH is negative.

(B) ΔH is positive.

(C) ΔS has a large positive value.

(D) ΔS has a small value of either sign.

Knowledge Required: (1) The meaning of the term *free energy*. (2) The relationship of enthalpy and entropy to free energy.

Thinking it Through: The thermodynamic function known as the Gibbs free energy is the relationship that predicts whether a chemical reaction is spontaneous. It depends on two values, the enthalpy of reaction and the product of the temperature and the entropy change for the reaction. For a reaction taking place at constant temperature, the relationship becomes $\Delta G = \Delta H - T\Delta S$. In general, the values of ΔH are in kJ and the values of ΔS are in joules per Kelvin, $J{\cdot}K^{-1}$.This means that unless the temperature is very high, so that the product of $T\Delta S$ becomes larger than the magnitude of ΔH, the spontaneity of a reaction is controlled by the sign of ΔH. If the sign of ΔG is negative, the reaction will be spontaneous in the forward direction. If ΔG is equal to zero, the reaction is at equilibrium because there is no driving force in either direction. If the sign of ΔG is positive, the reaction as written will be nonspontaneous. This question asks for the relationship of the size of ΔH to that of $T\Delta S$ in order to make a qualitative judgement about the value of the free energy. In choice **(A)**, even if ΔH is negative, the value of ΔG might become positive if the temperature were high and/or the entropy change were large enough. In choice **(B)**, ΔH is positive, which usually predicts a nonspontaneous reaction unless there is significant entropy change and high temperature conditions. In choice **(C)**, there is still the possibility that the value of $T\Delta S$ could control the reaction, even if the value of ΔH were negative. Only choice **(D)** gives the possibility of a relatively temperature independent value for the free energy change. If ΔS has a small value, no matter what the sign, then the product of the temperature and the entropy change will be a small number compared to the size of the enthalpy change.

EN-9 Which of the relationships is(are) true about water boiling in a container that is open to the atmosphere?

	Relationships
I	$\Delta H = 0$
II	$\Delta S = 0$
III	$\Delta G = 0$

(A) **I** only

(B) **III** only

(C) **I** and **II** only

(D) **II** and **III** only

Knowledge Required: (1) The meaning of the thermodynamic functions of enthalpy, entropy, and free energy. (2) The changes in thermodynamic relationships during change in state.

Thinking it Through: The normal boiling point of a liquid is the temperature at which the vapor pressure of the liquid is equal to 760 mmHg or 1 atmosphere pressure. When water is boiling, there is equilibrium between the rate at which water molecules are escaping the surface and the rate at which molecules are condensing. Considerable energy must be supplied to water for its molecules to have enough energy to escape the surface of the liquid, so ΔH cannot be equal to zero. This eliminates both choices **(A)** and **(C)** from consideration. The molecules in the vapor state are more random than the more ordered molecules in the liquid state, so ΔS also cannot be equal to zero. This eliminates choice **(C)** again, and now also choice **(D)**. Choice **(B)** is correct because it identifies the change in free energy as zero, a characteristic of an equilibrium state.

EN-10 For this reaction at 25 °C, $\Delta H^\circ = -1854$ kJ and $\Delta S^\circ = -236\ \mathrm{J{\cdot}K^{-1}}$.

$$\mathrm{CH_3COCH_3}(g) + 4\mathrm{O_2}(g) \rightarrow 3\mathrm{CO_2}(g) + 3\mathrm{H_2O}(l)$$

What is the value of ΔG° for this reaction?

(A) –1784 kJ **(B)** –1848 kJ **(C)** –1924 kJ **(D)** 68500 kJ

Knowledge Required: (1) The calculation of free energy from enthalpy and entropy data. (2) The correct use of units.

Thinking it Through: The free energy change for any reaction can be calculated using $\Delta G = \Delta H - T\Delta S$. To do this successfully, take careful note of the units.

$$\Delta G = -1854\ \mathrm{kJ} - 298\ \mathrm{K} \times \frac{-263\ \mathrm{J}}{\mathrm{K}} \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}$$

$$\Delta G = -1854\ \mathrm{kJ} + 70\ \mathrm{kJ}$$

$$\Delta G = -1784\ \mathrm{kJ}$$

This is choice **(A)**. Common errors in this type of calculation include forgetting to change the temperature from 25 °C to 298 K, resulting in choice **(B)**. It is also easy to make a sign error in the second part of the expression, carelessly making the product of two negatives values still a negative value; this produces the incorrect choice **(C)**. If you neglect to change joules to kilojoules, then you will combine 70,000 J with kJ and obtain the large value in choice **(D)**. This careless error should be easy to spot, for remember that for most combustion reactions, the magnitude of the enthalpy term provides the driving force for the reaction.

Practice Questions

1. When a 45.0 g sample of an alloy at 100.0 °C is dropped into 100.0 g of water at 25.0 °C, the final temperature is 37.0 °C. What is the specific heat of the alloy?

Specific Heat Data	
$H_2O(l)$	$4.184\ J\cdot g^{-1}\cdot {}^\circ C^{-1}$

(A) $0.423\ J\cdot g^{-1}\cdot {}^\circ C^{-1}$ **(B)** $1.77\ J\cdot g^{-1}\cdot {}^\circ C^{-1}$ **(C)** $9.88\ J\cdot g^{-1}\cdot {}^\circ C^{-1}$ **(D)** $48.8\ J\cdot g^{-1}\cdot {}^\circ C^{-1}$

2. When 68.00 J of energy are added to a sample of gallium that is initially at 25.0 °C, the temperature rises to 38.0 °C. What is the volume of the sample?

Data for Gallium, Ga	
specific heat	$0.372\ J\cdot g^{-1}\cdot {}^\circ C^{-1}$
density	$5.904\ g\cdot cm^{-3}$

(A) $2.38\ cm^3$ **(B)** $4.28\ cm^3$ **(C)** $14.1\ cm^3$ **(D)** $31.0\ cm^3$

3. A student mixes 100 mL of 0.50 M NaOH with 100 mL of 0.50 M HCl in a Styrofoam® cup and observes a temperature increase of ΔT_1. When she repeats this experiment using 200 mL of each solution, she observes a temperature change of ΔT_2. If no heat is lost to the surroundings or absorbed by the Styrofoam cup, what is the relationship between ΔT_1 and ΔT_2?

(A) $\Delta T_2 = 4\ \Delta T_1$ **(B)** $\Delta T_2 = 2\ \Delta T_1$ **(C)** $\Delta T_2 = 0.5\ \Delta T_1$ **(D)** $\Delta T_2 = \Delta T_1$

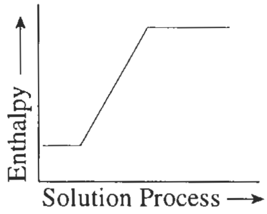
4. When a material in the liquid state is vaporized and then condensed to a liquid, the steps in the process are, respectively,

(A) exothermic and exothermic. **(B)** exothermic and endothermic.

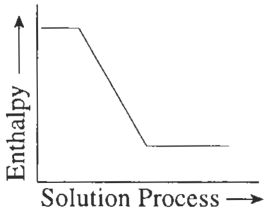
(C) endothermic and exothermic. **(D)** endothermic and endothermic.

5. When $Na_2S_2O_3\cdot 3H_2O$ dissolves in water, the solution gets cold. Which diagram best represents the change in enthalpy for the contents of the flask?

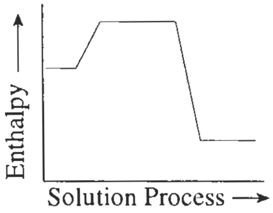
(A)



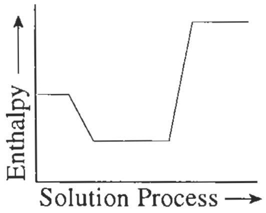
(B)



(C)



(D)



6. Calculate ΔH° = for the chemical reaction

$$Cl_2(g) + F_2(g) \rightarrow 2ClF(g)$$

Bond Energies, $kJ\cdot mol^{-1}$	
F–F	159
Cl–Cl	243
Cl–F	255

(A) −147 kJ **(B)** −108 kJ **(C)** +171 kJ **(D)** +912 kJ

7. More heat is derived from cooling one gram of steam at 100 °C to water at 50 °C than from cooling one gram of liquid water at 100 °C to 50 °C because

(A) the steam is hotter than the water.

(B) the steam occupies a greater volume than the water.

(C) the density of water is greater than that of steam.

(D) the heat of condensation is evolved.

8. Calculate ΔH for this gas phase reaction.

$$NH_3(g) + Cl_2(g) \rightarrow NH_2Cl(g) + HCl(g)$$

Bond Energies, $kJ\cdot mol^{-1}$

N–H	389	H–Cl	427
N–Cl	201	Cl–Cl	243

(A) –632 kJ **(B)** –188 kJ **(C)** +4 kJ **(D)** +431 kJ

9. Use the bond energies in the table to determine ΔH for the formation of hydrazine, N_2H_4, from nitrogen and hydrogen according to this equation.

$$N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$$

Bond Energies, $kJ\cdot mol^{-1}$

N–N	159	H–H	436
N=N	201	H–N	389
N≡N	941		

(A) –711 kJ **(B)** –98 kJ **(C)** +98 kJ **(D)** +711 kJ

10. A 1.00 g sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature increases by 6.12 °C. What is the molar heat of decomposition for ammonium nitrate?

Table of Data

Molar mass, NH_4NO_3	$80.0\ g\cdot mol^{-1}$
Calorimeter Constant	$1.23\ kJ\cdot {}^{\circ}C^{-1}$

(A) $-602\ kJ\cdot mol^{-1}$ **(B)** $-398\ kJ\cdot mol^{-1}$ **(C)** $7.53\ kJ\cdot mol^{-1}$ **(D)** $164\ kJ\cdot mol^{-1}$

11. In a bomb calorimeter, reactions are carried out at

(A) constant pressure. **(B)** constant volume.

(C) 1 atm pressure and 25 °C. **(D)** 1 atm pressure and 0 °C.

12. The standard enthalpy of formation, ΔH_f°, for nitrogen(IV) oxide, NO_2, is the enthalpy change for which reaction?

(A) $N(g) + 2O(g) \rightarrow NO_2(g)$ **(B)** $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$

(C) $\frac{1}{2}N_2O_4(g) \rightarrow NO_2(g)$ **(D)** $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$

13. The combustion of ammonia is represented by this equation.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \quad \Delta H^\circ_{rxn} = -904.8\ kJ$$

What is the enthalpy of formation of $NH_3(g)$?

Enthalpy of Formation Data

$NO(g)$	$+90.4\ kJ\cdot mol^{-1}$
$H_2O(g)$	$-241.8\ kJ\cdot mol^{-1}$

(A) $-449\ kJ\cdot mol^{-1}$ **(B)** $-46.1\ kJ\cdot mol^{-1}$ **(C)** $-184\ kJ\cdot mol^{-1}$ **(D)** $227\ kJ\cdot mol^{-1}$

14. The standard enthalpy change for the formation of silver chloride from its elements is _____than the enthalpy change for the formation of silver bromide.

Standard Enthalpies of Formation, 298 K	
$AgCl(s)$	$-127.1\ kJ\cdot mol^{-1}$
$AgBr(s)$	$-100.4\ kJ\cdot mol^{-1}$

(A) more exothermic **(B)** less exothermic

(C) more endothermic **(D)** less endothermic

15. What is the value of $\Delta H°$ for this reaction?

$$C_4H_4(g) + 2H_2(g) \rightarrow C_4H_8(g)$$

Enthalpies of Combustion	
$C_4H_4(g)$	$-2341\ kJ\cdot mol^{-1}$
$H_2(g)$	$-286\ kJ\cdot mol^{-1}$
$C_4H_8(g)$	$-2755\ kJ\cdot mol^{-1}$

(A) −158 kJ **(B)** −128 kJ **(C)** +128 kJ **(D)** +158 kJ

16. Given these values of $\Delta H°$:

$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$ $\Delta H° = -1077$ kJ

$H_2(g) + O_2(g) \rightarrow H_2O_2(l)$ $\Delta H° = -188$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H° = -286$kJ

What is the value of $\Delta H°$ for this reaction?

$$CS_2(l) + 6H_2O_2(l) \rightarrow CO_2(g) + 6\ H_2O(l) + 2SO_2(g$$

(A) $-1175\ kJ\cdot mol^{-1}$ **(B)** $-1151\ kJ\cdot mol^{-1}$ **(C)** $-1665\ kJ\cdot mol^{-1}$ **(D)** $-3921\ kJ\cdot mol^{-1}$

17. Use the standard enthalpies of formation in the table to calculate $\Delta H°$ for this reaction.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$

Substance	$\Delta H_f°$, $kJ\cdot mol^{-1}$
$CrO_4^{2-}(aq)$	−881.2
$Cr_2O_7^{2-}(aq)$	−1490.3
$H^+(aq)$	0
$H_2O\ (l)$	−285.8

(A) +272.1 kJ **(B)** +13.7 kJ **(C)** −13.7 kJ **(D)** −272.1 kJ

18. What is the value of $\Delta H°$ for this reaction?

$$3H_2(g) + O_3(g) \rightarrow 3H_2O(l)$$

Reaction	ΔH, kJ
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	−286 kJ
$3O_2(g) \rightarrow 2O_3(g)$	+271 kJ

(A) −15 kJ **(B)** −558 kJ **(C)** −722kJ **(D)** −994 kJ

19. Calculate the enthalpy of combustion of ethylene, C_2H_4, at 25 °C and one atmosphere pressure.

$$C_2H_4(g)+ 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

Compound	$\Delta H_f°$, $kJ\cdot mol^{-1}$
$C_2H_4(g)$	+52.3
$H_2O(l)$	−285.8
$CO_2(g)$	−393.5

(A) −1411 kJ **(B)** −1254 kJ **(C)** −732kJ **(D)** −627 kJ

20. Use the given heats of formation to calculate the enthalpy change for this reaction.

$$B_2O_3(s) + 3COCl_2(g) \rightarrow 2BCl_3(g) + 3CO_2(g)$$

Compound	**ΔH_f°, kJ·mol^{-1}**
$B_2O_3(s)$	–1272.8
$COCl_2(g)$	–218.8
$BCl_3(g)$	–403.8
$CO_2(g)$	–393.5

(A) 694.3 kJ **(B)** 354.9 kJ **(C)** –58.9 kJ **(D)** –3917.3 kJ

21. Using the given thermochemical data, what is ΔH° for this reaction?

$$2CH_3OH(l) + O_2(g) \rightarrow HC_2H_3O_2(l) + 2H_2O(l)$$

Compound	**ΔH_f°, kJ·mol^{-1}**
$CH_3OH(l)$	–238
$HC_2H_3O_2(l)$	–487
$H_2O(l)$	–286

(A) 583 kJ **(B)** 535 kJ **(C)** –583 kJ **(D)** –535 kJ

22. What is the enthalpy change for this reaction?

$$Hg(l) + 2Ag^+(aq) \rightarrow Hg^{2+}(aq) + 2Ag(s)$$

Compound	**ΔH_f°, kJ·mol^{-1}**
$Ag^+(aq)$	+105.6
$Hg^{2+}(aq)$	+171.1

(A) +65.5 kJ **(B)** +40.1 kJ **(C)** –40.1 kJ **(D)** –65.5 kJ

23. For which of these processes is the value of ΔS expected to be negative?

I. Sugar is dissolved in water.
II. Steam is condensed.
III. $CaCO_3$ is decomposed into CaO and CO_2.

(A) I only **(B)** I and III only

(C) II only **(D)** II and III only

24. For which process is the entropy change per mole the largest at constant temperature?

(A) $H_2O(l) \rightarrow H_2O(g)$ **(B)** $H_2O(s) \rightarrow H_2O(g)$

(C) $H_2O(s) \rightarrow H_2O(l)$ **(D)** $H_2O(l) \rightarrow H_2O(s)$

25. In which process is entropy *decreased*?

(A) dissolving sugar in water **(B)** expanding a gas

(C) evaporating a liquid **(D)** freezing water

26. When a liquid evaporates, which is true about the signs of the enthalpy and entropy changes?

(A) ΔH is positive, ΔS is positive **(B)** ΔH is positive, ΔS is negative

(C) ΔH is negative, ΔS is positive **(D)** ΔH is negative, ΔS is negative

27. A particular chemical reaction has a negative ΔH and a negative ΔS. Which statement is correct?

(A) The reaction is spontaneous at all temperatures.

(B) The reaction is nonspontaneous at all temperatures.

(C) The reaction becomes spontaneous as temperature increases.

(D) The reaction becomes spontaneous as temperature decreases.

28. When solid NH_4NO_3 is dissolved in water at 25 °C, the temperature of the solution decreases. What is true about the signs of ΔH and ΔS for this process?

(A) ΔH is negative, ΔS is positive

(B) ΔH is negative, ΔS is negative

(C) ΔH is positive, ΔS is positive

(D) ΔH is positive, ΔS is negative

29. For the process $O_2(g) \rightarrow 2O(g)$, $\Delta H^\circ = +498$ kJ. What would be predicted for the sign of ΔS_{rxn} and the conditions under which this reaction would be spontaneous?

	ΔS_{rxn}	**Spontaneous**
(A)	positive	at low temperatures only
(B)	positive	at high temperatures only
(C)	negative	at high temperatures only
(D)	negative	at low temperatures only

30. For which reaction, carried out at standard conditions, would both the enthalpy and entropy changes drive the reaction in the same direction?

(A) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H = -571.1$ kJ

(B) $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$ $\Delta H = -822.0$ kJ

(C) $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H = +67.7$ kJ

(D) $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)\ (l)$ $\Delta H = +92.4$kJ

Practice Questions

1. A compound is found to consist of 34.9% sodium, 16.4% boron and 48.6% oxygen. What is its simplest formula?

(A) $NaBO_2$ **(B)** $NaBO_3$ **(C)** $Na_2B_4O_7$ **(D)** Na_3BO_3

2. Upon analysis, a compound is found to contain 22.8% sodium, 21.8% boron, and 55.4% oxygen. What is its simplest formula?

(A) $NaBO$ **(B)** NaB_2O_5 **(C)** $Na_2B_4O_7$ **(D)** Na_3BO_4

3. A 4.08 g sample of a compound of nitrogen and oxygen contains 3.02 g of oxygen. What is the empirical formula?

(A) NO **(B)** NO_2 **(C)** N_2O **(D)** N_2O_5

4. What is the percent by mass of oxygen in $Ca(NO_3)_2$?

(A) 29.3 % **(B)** 47.1 % **(C)** 58.5 % **(D)** 94.1 %

5. Which of these compounds contains the greatest percentage of nitrogen?

Formula	Molar Mass
$C_6H_3N_3O_7$	229. g·mol^{-1}
CH_4N_2O	60.1 g·mol^{-1}
$LiNH_2$	23.0 g·mol^{-1}
$Pb(N_3)_2$	291. g·mol^{-1}

(A) $C_6H_3N_3O_7$ **(B)** CH_4N_2O **(C)** $LiNH_2$ **(D)** $Pb(N_3)_2$

6. What mass of carbon is present in 0.500 mol of sucrose ($C_{12}H_{22}O_{11}$)?

Formula	Molar Mass
$C_{12}H_{22}O_{11}$	342 g·mol^{-1}

(A) 60.0 g **(B)** 72.0 g **(C)** 90.0 g **(D)** 120. g

7. How many atoms are in 1.50 g of Al?

(A) 0.0556 **(B)** 18.0 **(C)** 3.35×10^{22} **(D)** 2.44×10^{25}

8. A sample of a compound of xenon and fluorine contains molecules of a single type; XeF_n, where n is a whole number. If 9.03×10^{20} of these XeF_n molecules have a mass of 0.311 g, what is the value of n?

(A) 2 **(B)** 3 **(C)** 4 **(D)** 6

9. What mass of carbon is present in 1.4×10^{20} molecules of sucrose ($C_{12}H_{22}O_{11}$)?

Formula	Molar Mass
$C_{12}H_{22}O_{11}$	342 g·mol^{-1}

(A) 1.7×10^{21} g **(B)** 2.0×10^{22} g **(C)** 3.3×10^{-2} g **(D)** 2.8×10^{-3} g

10. A 2.000 g sample of an unknown metal, M, was completely burned in excess O_2 to yield 0.02224 mol of the metal oxide, M_2O_3. What is the metal?

(A) Y **(B)** Ca **(C)** Al **(D)** Sc

Answers to Study Questions

1. B
2. A
3. A
4. A
5. D
6. B
7. C
8. D
9. B
10. A

Answers to Practice Questions

1. B
2. A
3. D
4. C
5. A
6. B
7. D
8. C
9. C
10. A
11. B
12. B
13. B
14. A
15. A
16. C
17. C
18. D
19. A
20. C
21. C
22. C
23. C
24. B
25. D
26. A
27. D
28. C
29. B
30. C